# Methanol Conversion to Light Olefins over Commercial Zeolites

by

Usman Aliyu El-Nafaty

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

**MASTER OF SCIENCE**

In

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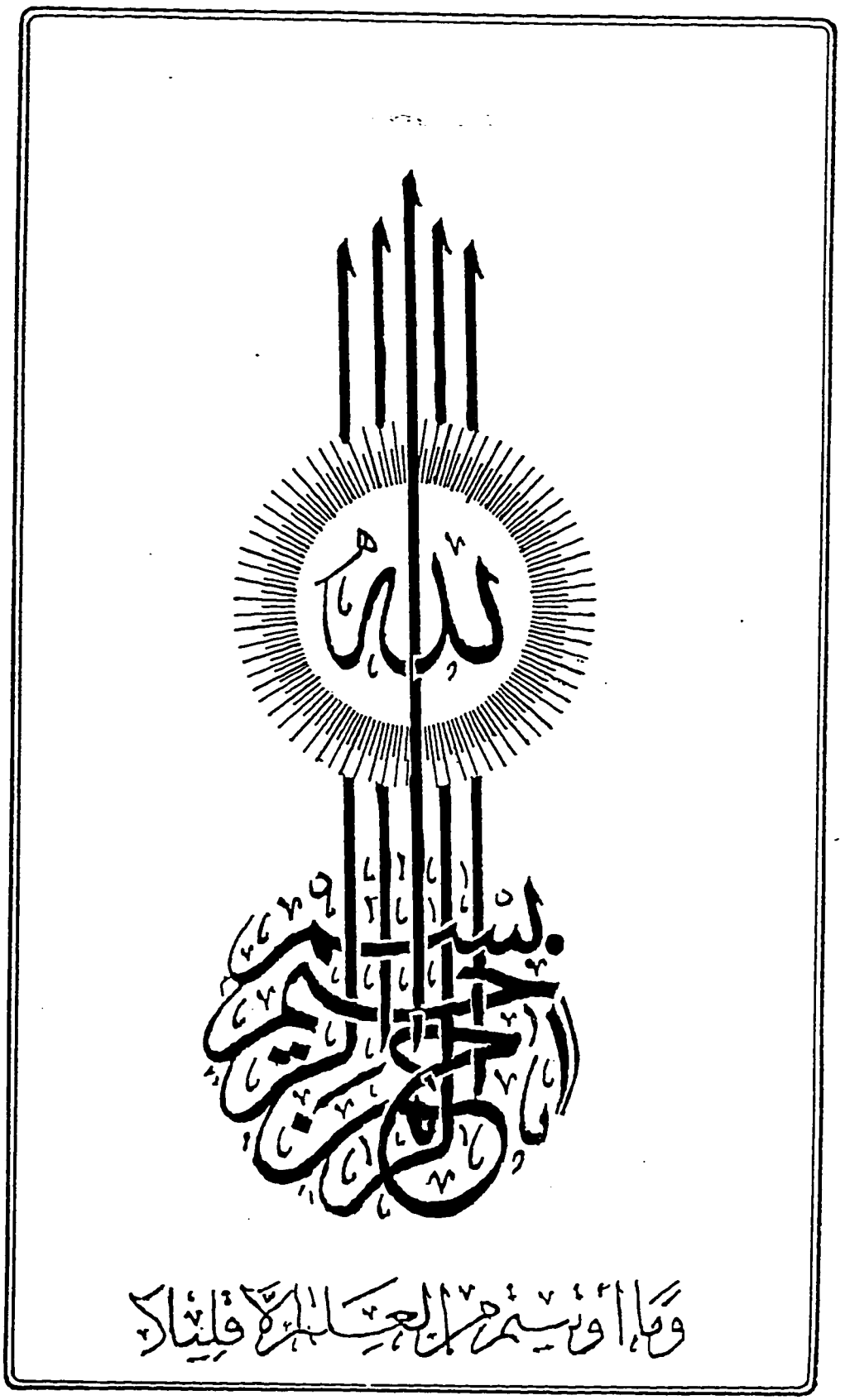
بسم الله الرحمن الرحيم
وما أوتيتم من العلم إلا قليلا

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN, SAUDI ARABIA

COLLEGE OF GRADUATE STUDIES

This thesis, written by Mr. Usman Aliyu El-Nafaty under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering.



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*Dedicated to:*

*My Parents, Wife and Daughter*

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# ABSTRACT

The conversion of methanol to light olefins (MTO) over commercial narrow pore Silicoaluminophosphate SAPO-34, and pentasil type ZSM-5 and Silicalite S-115, was studied in a fixed bed tubular reaction system. Nitrogen was used as carrier gas. Experiments were carried out at various temperatures, space velocities (WHSV) and methanol-to-nitrogen (wt) ratio to study their effects on catalyst activity, selectivity, product distribution and coke deposition. ZSM-5 and S-115 were modified by impregnation with various metal elements to investigate their effects on catalyst active life time and selectivity to lower olefins. At 400 °C and 4 $hr^{-1}$ WHSV SAPO-34 exhibited higher initial selectivity to lower olefins than both ZSM-5 and S-115 but also deactivated more rapidly (< 2hrs). This was attributed to the catalyst's narrow pore size which enhanced coke formation leading to poisoning of active sites and blockade of pore channel entrances. The optimum operating conditions for S-115 and ZSM-5 were found to be 375 °C and 450 °C respectively at 4 $hr^{-1}$ WHSV and 2.67 methanol-to-nitrogen (wt) ratio. S-115 showed higher overall selectivity to olefins than ZSM-5 at optimum conditions. Active life-on-stream was also longer for S-115 than ZSM-5 with 58.1 and 25.5 hr respectively. Since both zeolites have identical pore-sizes and structures, the better performance of S-115 was attributed to its higher silica/alumina ratio of 300 as compared to ZSM-5 which had a silica/alumina ratio of 40. Modification of the two zeolites with various elements showed the degree of selectivity to light olefins to vary according to the modifying element. With S-115, the selectivity was found to vary according to the order Ba > La > Ag > Cu > Ca > Sr > Ga > Cd > In, while for ZSM-5, the selectivity decreased in the order In > Ag > Cu > Cd. Optimum Ba-loading on S-115 for high olefin yield was found to be 5.2% by impregnation and 0.03% by ion-exchange.

# الخلاصـــــة

تم في هذا البحث دراسة عملية تحويل الميثانول الى الأليفينات الخفيفة باستخدام حفازات صناعية من نوع السيليكا - ألومينا - فوسفات (SAPO-34) والبنتازيل (ZSM-5) والسيليكالايت (S-115) وذلك في جهاز تفاعل أنبوبي تم تصميمه خلال هذه الدراسة . ولقد استخدم النيتروجين كغاز حامل خلال التفاعل . أجريت التجارب المختبرية عند درجات حرارة وسرعات تدفق ومعدلات ميثانول الى نيتروجين مختلفة وذلك لدراسة أثر هذه العوامل على نشاط الحفاز وانتقائيته وتوزيع المنتجات وترسب الكربون . لقد تم تعديل الحفازات ZSM-5 و S-115 بطريقة التشبع باستخدام عناصر معدنية مختلفة لمعرفة تأثير هذه العناصر على العمر النشط للحفاز وانتقائيته الى الأليفينات الخفيفة . وأظهر الحفاز SAPO-34 عند درجة حرارة ٤٠٠ درجة مئوية وسرعة تدفق ٤/ساعة انتقائية عالية الى الأليفينات الخفيفة في بداية التفاعل مقارنة مع حفازي ZSM-5 و S-115 ولكن الخواص الحفزية لـ SAPO-34 تدهورت بصورة سريعة ( أقل من ساعتين ) . والسبب في هذا التدهور يعود الى ضيق المسامات في الحفاز المذكور والتي سرّعت من ترسب الكربون وبالتالي الى تسمم المواقع النشطة وانسداد مداخل مسامات الحفاز . ان عمليات التشغيل المثلى لحفاز S-115 وحفاز ZSM-5 هي ٣٧٥ درجة مئوية و٤٥٠ درجة مئوية على التوالي وذلك عند سرعة تدفق تعادل ٤/ساعة ومعدل الميثانول الى النيتروجين تعادل ٢ر٦٧ . لقد أظهر الحفاز S-115 انتقائية إجمالية مرتفعة للأليفينات مقارنة مع حفاز ZSM-5 عند عوامل التشغيل المثلى . وبالنسبة للعمر النشط للحفاز فقد أظهرت النتائج أن حفاز S-115 إستمر لفترة ١ر٥٨ ساعة مقارنة بـ ٥ر٢٥ ساعة لحفاز ZSM-5 . وبالرغم من أن كلا الحفازين لديهما تركيبات ومسامات مشابهة ، فإن الأداء الأفضل للزيولايت S-115 يمكن إرجاعه الى معدل السيليكا للألومينا المرتفع الذي يعادل ٣٠٠ مقارنة مع المعدل المنخفض في حفاز ZSM-5 والذي يعادل ٤٠ . إن تعديل كلا الحفازين بعناصر مختلفة أدى الى تغير في الانتقائية الحفزية للأليفينات الخفيفة وذلك حسب تغير عناصر التعديل المستخدمة . فبالنسبة لـ S-115 فقد أظهرت النتائج أن الانتقائية تتغير حسب الترتيب التالي : الباريوم > لانثانيوم > الفضة > النحاس > الكالسيوم > السترونشيوم > الجاليوم > الكادميوم > الإنيديوم . في حين أن الإنتقائية الحفزية لـ ZSM-5 قد تناقصت حسب الترتيب التالي : الإنيديوم > الفضة > النحاس > الكادميوم . ان الكمية المثلى للباريوم والتي استخدمت في تعديل الحفاز S-115 وذلك بالنسبة لإنتاج الأليفينات فقد أظهرت النتائج أن الكمية هي ٢ر٥٪ باستخدام طريقة التشبع و ٣ر٠٪ بطريقة التبادل الأيوني .

# CHAPTER 1. INTRODUCTION

## *1.1 BACKGROUND*

Light Olefins ( Ethylene, Propylene, and Butenes) are fundamental raw materials in the petrochemical Industry from which a multitude of intermediate and end products (mainly polymeric materials) are produced. At present, the bulk amount of light olefins is produced from natural gas and naphtha by cracking processes.

Methanol is another major raw material in the chemical industry and forms one of the largest volume chemicals in the world{1} . Since technology for the production of methanol from natural gas, coal or virtually any carbon source is well established{2}, conversion of methanol to light olefins will serve a new link for transformation of fossil fuels into valuable hydrocarbons. Of more economic significance however, is the present surplus of Methanol in the world market{3} and perhaps in the future as well. Saudi Arabia produces 1.41 million metric tons per annum {4} which accounts for about 7% of the world total methanol and at present almost all of it is exported. Conversion of methanol to light olefins is therefore a potential avenue both for local utilization as well as for tackling the problem of anticipated surplus.

Interest in such area has grown increasingly from the early seventies when Mobil Co. discovered a zeolite (ZSM-5) capable of transforming methanol to gasoline (MTG) range hydrocarbons{5}. An overall scheme for the conversion reaction is depicted in Figure 1.1.

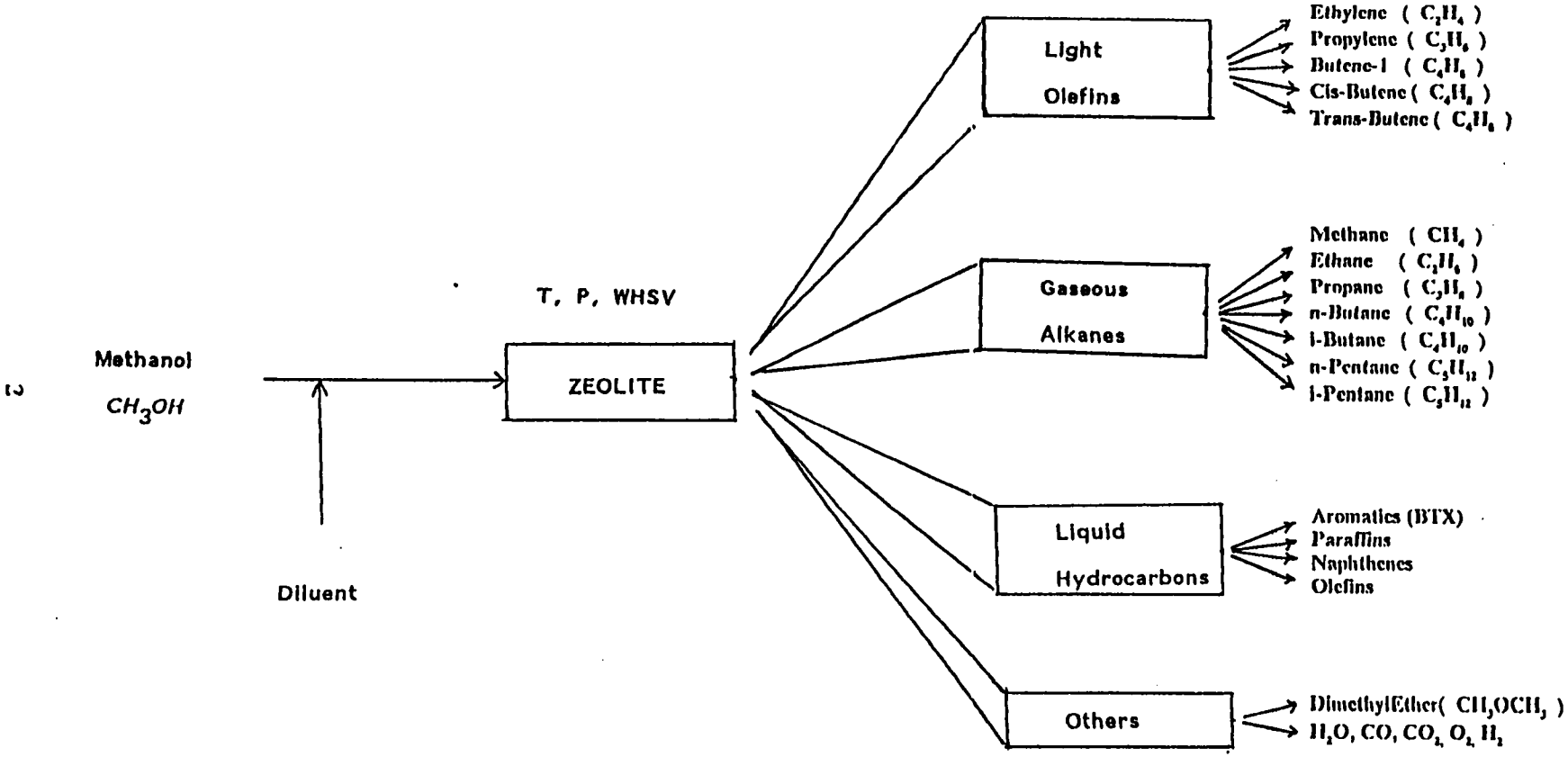



**Figure 1.1. :** Reaction Scheme For Methanol Conversion

The discovery of the MTG process itself occurred by accident while two teams of Mobil scientists were working on unrelated projects {6}. One group was trying to convert methanol to ethylene oxide and the other attempting to methylate isobutane with methanol - both in the presence of ZSM-5. Instead, a mixture of "unwanted" hydrocarbons were obtained which turned out to be gasoline range paraffins and aromatics. Research was then directed in this line culminating in the commissioning of the Newzealand MTG process in 1985 {7,8}. Subsequent investigation on the chemistry of the MTG reaction {9-13} showed olefins to be intermediate species in the transformation of methanol to higher hydrocarbons. This understanding, became the initiating point that gave rise to a new dimension of research into converting methanol to olefins (MTO).

Since then, numerous works on methanol-to-hydrocarbons conversion have been published. Nevertheless most of the work done concerned production of hydrocarbons in general and studies on selective conversion to light olefins and in particular to specific olefins seem relatively scarce.

The overall reaction path may be represented {11} by equation 1 below :

$$\frac{n}{2}[2CH_3OH \rightarrow CH_3OCH_3 + H_2O] \xrightarrow{-nH_2O} C_nH_{2n} \rightarrow n[CH_2] \quad \text{--- (1)}$$

| Methanol | Dimethyl Ether | Water | Olefins | Paraffins + Aromatics |
|---|---|---|---|---|

where $[CH_2]$ = average formula of an aromatic-paraffin mixture

Apart from the autocatalytic nature of the reactions, the reaction steps are in general, kinetically coupled. The product distribution is influenced by catalyst properties as well as various reaction parameters. Depending upon catalyst type, reaction parameters such as temperature, pressure, and space velocity, might have profound effects on product distribution. The catalyst Bronsted acidity, silica/alumina ratio, crystallite size, and even synthesis procedure play major role in determining catalyst activity and selectivity. Methanol dilution with various substances such as $H_2O$, $O_2$, $H_2$, CO, $CO_2$, NO, $N_2$ etc , was found to have significant effect on the product spectrum in the MTO reaction. The major issue in this reaction is that these parameters are strongly interrelated and the problem of identifying the right combination of parameters that favour selective conversion to light olefins is still a challenge. Several approaches to this problem have been suggested; most of which hinge on finding means to decouple the oligomerization step in the reaction sequence. In general however, it has been observed that reduction of contact time, low acidity, water dilution and modification of catalyst with suitable promoters, enhanced the selectivity to light olefins{14}.

### *1.2 SCOPE AND OBJECTIVES*

Our investigation comprised, the study of the conversion of methanol to light olefins (MTO) using three commercial catalysts: Silicoaluminophosphate SAPO-34, Silicalite S-115 and Zeolite ZSM-5. Emphasis was given to the catalyst activity and selectivity. Experiments were carried out in a fixed bed tubular continuous flow bench scale reaction unit. Results obtained from such

set-up reflected real engineering process more closer than micro- or pulse reactor unit, used by most investigators. The objectives of this study were:

1. To asses the activity and selectivity of three commercial catalysts ZSM-5, SAPO-34 and Silicalite S-115 on the conversion of Methanol to Olefins (MTO) in a continuous flow bench scale reaction unit.

2. To study the effects of temperature, space velocity and feed dilution, on the activity and selectivity of selected catalyst.

3. To study the effects of promoters on the performance of the selected catalyst in the MTO conversion reaction.

# CHAPTER 2. LITERATURE REVIEW

## 2.1 Review of Catalysts used in MTO.

Zeolites are porous crystalline aluminosilicates, composed of $AlO_4$ and $SiO_4$ tetrahedra interconnected through shared oxygen atoms, forming a three dimensional network {15}. The framework structures having well defined pore geometries enclose cavities occupied by large ions and water molecules both of which have considerable freedom of movement permitting ion-exchange and reversible dehydration. The crystallographic unit cell is generally represented as :

$$M_{x/n}[(AlO_2)_x(SiO_2)_y].zH_2O$$

where:

M = Cation of valence n

z = Number of molecules of water of hydration

x = Number of $AlO_2$ molecules

y = Number of $SiO_2$ molecules

y/x generally ranges between 1 - 5 {16}

The unique property of zeolites is their well defined pore and channel structure which leads to diffusional constraints that limit the size and shape of both reactant and product molecules that can be processed. This

phenomenon is termed "shape-selectivity". Reactant selectivity occurs when access to intracrystalline catalytic sites is afforded to one class of reactant molecules and denied to another, based on shape and size. Product selectivity on the other hand takes place when the pore system permits only the formation of a mixture of product with limited range of molecular size and shape that can diffuse out. Bulky products, if formed, are either converted to less bulky molecules (e.g., by equilibration), or eventually deactivate the catalyst by blocking the pore{17}.

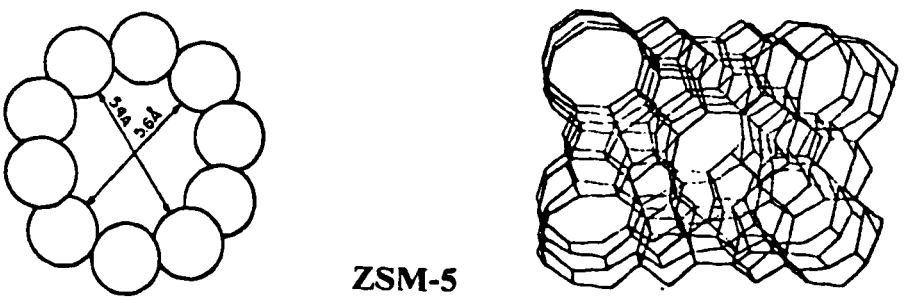
The catalytic activity of zeolites is associated with the presence of acidic groups within the intracrystalline surface {18}. The acid strength and number of acidic centers can be controlled either during preparation or by subsequent ion-exchange. The channels and cavities in zeolites can have various diameters depending on the framework structure formed by the $SiO_4$ and $AlO_4$ tetrahedra. The catalytically most important classes of zeolites however, are those having pore diameters characterized by 8- , 10-, and 12-ring of oxygen atoms (Figure 2.1).

Acidic forms of various narrow pore (8-ring), medium pore(10-ring or pentasil type), and wide pore(12-ring) zeolites have been used to convert methanol to olefins and other hydrocarbons. Table 2.1 shows a representative data on methanol conversion over zeolites of different pore sizes {15}. Small pore ( 4.3Å) erionite, produces only lower molecular weight hydrocarbons. It does not sorb benzene and therefore cannot produce aromatics. The intermediate pore ( 6Å ) ZSM-5 and ZSM-11,

**Figure 2.1 :** Pore Structures of Common Zeolites Used in Methanol Conversion to Olefins

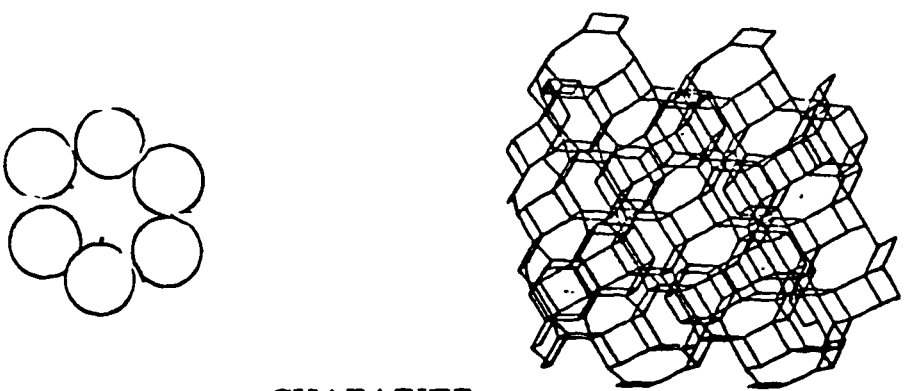

**FAUJASITE**

$(Na_2, Ca, Mg)_{29}Al_{58}Si_{134}O_{384} \cdot 240\ H_2O$




**ZSM-5**

$Na_nAl_nSi_{96-n}O_{192} \cdot 16\ H_2O$ with $n < 27$



**CHABAZITE**

$Ca_6Al_{12}Si_{24}O_{72} \cdot 40\ H_2O$

Table 2.1 : Methanol Conversion to Hydrocarbons over Various Zeolites (370 °C, 1 atm, 1 LHSV) {15}

| PRODUCT | Hydrocarbon distribution (wt %) in | | | | |
|---|---|---|---|---|---|
| | Erionite | ZSM-5 | ZSM-11 | ZSM-4 | Mordenite |
| $C_1$ | 5.5 | 1.0 | 0.1 | 8.5 | 4.5 |
| $C_2$ | 0.4 | 0.6 | 0.1 | 1.8 | 0.3 |
| $C_2^{2-}$ | 36.3 | 0.5 | 0.4 | 11.2 | 11.0 |
| $C_3$ | 1.8 | 16.2 | 6.0 | 19.1 | 5.9 |
| $C_3^{2-}$ | 39.1 | 1.0 | 2.4 | 8.7 | 15.7 |
| $C_4$ | 5.7 | 24.2 | 25.0 | 8.8 | 13.8 |
| $C_4^{2-}$ | 9.0 | 1.3 | 5.0 | 3.2 | 9.8 |
| $C_5^+$ aliphatics | 2.2 | 14.0 | 32.7 | 4.8 | 18.6 |
| $A_6$* | - | 1.7 | 0.8 | 0.1 | 0.4 |
| $A_7$ | - | 10.5 | 5.3 | 0.5 | 0.9 |
| $A_8$ | - | 18.0 | 12.4 | 1.3 | 1.0 |
| $A_9$ | - | 7.5 | 8.4 | 2.2 | 1.0 |
| $A_{10}$ | - | 3.3 | 1.5 | 3.2 | 2.0 |
| $A_{11}^+$ | - | 0.2 | .7 | 26.6 | 15.1 |

* A = aromatics.

truncate the hydrocarbon distribution at $C_{11}$, while the large pore (8Å) ZSM-4, and mordenite which can accommodate molecules as bulky as hexamethylbenzene, produces the compound along with other aromatics.

Chen and Garwood {19} and Langner {20}, also reported works on various aspects of shape selectivity of zeolites with different pore structures. More thorough treatment on zeolite shape selectivity can be found in references {21-23}.

### *2.1.1. Methanol Conversion Over Narrow Pore Zeolites*

The principle of shape selective catalysis has been applied to convert methanol to small molecular hydrocarbons using catalysts with narrow channel sizes. Chang et al.{13}, reported data on methanol conversion over narrow pore zeolites erionite, chabazite, zeolite-T and ZK-5. At 339 – 538 °C, the products were mainly $C_2 - C_4$ Olefins. Methanol conversion over zeolite-T was also studied by Ceckiewicz {24}. At 400 °C, about 90% conversion was achieved and the product contained mostly $C_2 - C_5$ straight chain hydrocarbons with 38 wt.% $C_2H_4$ and 39 wt.% $C_3H_6$. Fleckenstein et al.{25}, studied the conversion of methanol over natural erionite/chabazite zeolites (Zeolon-500) and synthetic erionite/offrerite mixtures (T-Zeolites). Reaction was carried out at 280 – 450 °C, and selectivities to $C_2 - C_4$ olefins of over 80% was obtained.

The more recent class of small pore zeolites used in the methanol conversion reaction are those belonging to the silicoaluminophosphate (SAPO) series of crystalline molecular sieves {26}. Kaiser {27}, reported using SAPO-17 and SAPO-34 to convert methanol to light olefins. At 375 - 450 °C, and 0.8 – 0.87 $hr^{-1}$ WHSV, a methanol feedstock consisting of 70/30 (wt%) water/methanol mixture was essentially completely converted to hydrocarbon products with combined molar selectivities to light olefins totalling 87 - 96%.

High temperature conversion of methanol to olefins over the hydrogen form of SAPO-34 (HSAPO-34) was investigated by Liang et al. {28} and Li et al. {29}. Reaction was carried out at 530°C and selectivity with respect to $C_2^-$ – $C_4^-$ of about 89% was obtained. The catalyst exhibited higher selectivity and stability than erionite and HSAPO-5 zeolites. Other narrow pore zeolites utilized include ZSM-34 {30,31}, cation-exchanged chabazites {32}, offrerite {33}, and erionite-offrerite {34,35}.

The major obstacle in applying this class of zeolites however lies in their high rates of coke formation leading to short active lifetime and generally, incomplete methanol conversion under commercial conditions.

### *2.1.2 Methanol Conversion Over Medium Pore Zeolites*

Medium pore (or pentasil type) zeolites are by far the most widely used catalysts in converting methanol to hydrocarbons. They have been

found to be more effective for this reaction {15}. Their framework structure has intersecting ten-membered ring channel systems with pore sizes intermediate between the eight-membered ring zeolites such as type-A zeolite and the twelve-membered ring zeolites of the faujasite type X, Y {36}. Extensive work has been done on converting methanol to hydrocarbons using ZSM-5 and related zeolites{25, 37-49}. The unique catalytic activity of ZSM-5 zeolites have been attributed to their crystal structure and acidic properties. Unlike the small and wide pore zeolites, this class of zeolites has channel pathways of uniform diameters free from the so-called "cage effects".

Chang et al. {40}, studied the methanol conversion reaction over ZSM-5 at various temperatures and methanol partial pressures. Depending upon the zeolite formulation ($SiO_2/Al_2O_3$ ratio) and reaction conditions , selectivities to lower olefins of 30 - 80% was achieved. Wu and Kaeding {41}, carried out similar investigation using hydrogen form of the zeolite (H-ZSM-5) with feedstocks consisting of either pure methanol or methanol diluted with water. At 100 % conversion, the products formed contained 1.8-50% $C_2H_4$ , 1.5-34% $C_3H_6$, and 0-27% $C_4H_8$. Young {50}, also reported converting methanol feeds containing various amounts of methanol in combination with different types of diluents over ZSM-5. Total $C_2^-$ - $C_4^-$ molar selectivity as high as 70% was obtained.

The amount of olefins formed over a zeolite under a set of reaction conditions has been a critical problem since olefins are intermediate products in the methanol conversion reaction. Thus they can easily react

with other species to form saturated paraffins and naphthenes or oligomerate and homologate to produce higher olefins and aromatics{51,52,20}.

Medium pore ZSM-5 was originally developed to convert methanol to gasoline range hydrocarbons {51}. To enhance higher selectivity to light olefins however, the zeolite framework structure and composition need to be modified. Techniques applied to improve the zeolite characteristics for high olefin formation include a) increasing shape selectivity by reducing apparent pore size of the zeolite through controlled incorporation of various substances in the zeolite channels and cavities; b) raising the $SiO_2/Al_2O_3$ ratio to decrease the catalyst's Bronsted acidity thereby limiting the reaction sequence at the olefin stage and suppressing formation of higher hydrocarbons {13,40,53,54}; and c) substituting the Al ingredient with various metal salts at the synthesis stage of gel formation to produce metallosilicates of identical pentasil pore-opening structure as ZSM-5 {55,56}.

Rodewald {57}, applied the first technique to improve the selectivity of ZSM-5 to lower olefins. Silica (7.4%) was deposited in the pores of the zeolite by impregnation with a solution of methylhydrogensilicone. At 370°C and $1hr^{-1}$ LHSV, methanol was converted to the product mixture shown in Table 2.2. As can be seen, selectivity to light olefins increased from 2.8% with untreated ZSM-5 to about 55.7% over the silanated zeolite. Kaeding and Butter {30} reacted methanol over phosphorus-modified ZSM-5. At 100% conversion, selectivity to $C_2 - C_4$ olefins of up

Table 2.2 : Methanol Conversion To Hydrocarbons Over ZSM-5. Effect of Zeolite Silanation (370 °C, 1 LHSV) {13}

| Hydrocarbon Product wt(%) | Untreated ZSM-5 | Salinated ZSM-5 |
|---|---|---|
| Methane | 1.0 | 1.3 |
| Ethane | 0.6 | 0.0 |
| Ethylene | 0.5 | 26.2 |
| Propane | 16.2 | 2.4 |
| Propylene | 1.0 | 18.7 |
| Butane | 24.2 | 5.4 |
| Butenes | 1.3 | 10.8 |
| $C_5^+$ Aliphatics | 14.0 | 16.0 |
| Aromatics | 41.2 | 19.2 |
| | 100 | 100 |

to 70% was obtained. Zatorski et al. {58}, modified H-ZSM-5 by treatment with oxalates or nitrate compounds of zinc (Zn), cerium (Ce), titanium (Ti), potassium (K), rhodium (Rh), cobalt (Co), zirconium (Zr), chromium (Cr), aluminium (Al), magnesium (Mg) and orthophosphoric acid. Other workers {52} applied the ion-exchange technique to incorporate metals such as berylium (Be), calcium (Ca), neodymium (Nd), lead (Pb), thorium (Th), niobium (Nb), molybdenum (Mo), Boron (B), or nickel (Ni) into the crystal lattice of the zeolite framework structure. The various modified catalysts exhibited different activities and selectivities to olefins in methanol conversion. Balkrishnan et al. {59} noted that although tortuosity in the zeolite channels is increased as a result of the modifications, the observed higher selectivities of some of the metal loaded zeolites was attributed more to alteration in surface acidity than to any steric effect.

Romanikov et al. {60}, investigated the influence of increasing $SiO_3/Al_2O_3$ ratio of ZSM-5 on the selectivity to light olefins. By varying the ratio from 24 to 540, the selectivity increased from 70.8% to 91.6%.

Methanol conversion over synthesized metallosilicates of the pentasil pore structure was reported by Inui et al. {56,61}. The product distribution over this class of zeolites changed with the metal type even at small concentration (eg Si/Metal ratio of 3200). The degree of selectivity to olefins was found to vary according to the order:

$$Ga = Cr < V < Sc < Ge < Mn < La = Al$$
$$< Ni < Zr = Ti < Fe < Co = Pt$$

Silicates of Fe, Co, and Pt are more effective for conversion of methanol to lower olefins than Al-silicate (H-ZSM-5), whereas Ga- , V- and Cr-silicates convert methanol mainly to gasoline and aromatics. Hocldrich et al. {62}, carried out similar investigation to compare the relative performance of Aluminosilicates (Al-silicate) and Borosilicates (B-silicate) in converting methanol to hydrocarbons. B-silicate zeolites possessed lower activity, and longer life on stream but exhibited higher selectivity to propene than Al-silicate (ZSM-5). Modification of the B-zeolites with hydrofluoric acid (HF), hydrochloric acid (HCl), aluminium oxide and silicon oxide lead to a significant increase in the active life on stream and selectivity to lower olefins. This was attributed to the improved cracking property and lower coking tendency of the modified zeolites. Romanikov et al.{60}, also studied the selectivity of B-, Al-, and Ga-silicates in converting methanol to light olefins. Under the reaction conditions, Ga-silicates exhibited similar behavior as Al-silicates whereas pure B-silicate zeolite with $Al_2O_3$ as admixture, converted methanol mainly to dimethylether.

Silicalites are another class of highly siliceous zeolites found active in converting methanol to olefins. They have skeletal structures very similar to that of ZSM-5 {63,64}. Though these zeolites posses the basic properties required for converting methanol , very little work has been reported on their use for this reaction particularly on efforts to improve

olefin selectivity. The high silica/alumina ratio characteristic of these zeolites make them less active for producing aromatics and higher hydrocarbons and hence more selective to low molecular weight hydrocarbons. This was confirmed by Anderson et al. {37}, who reacted methanol over silicalite and H-ZSM-5 at 400°C. The reaction products for silicalite contained about 76% $C_1 - C_5$ aliphatics as compared to 21.6% for H-ZSM-5.

Anthony and Thomas {65} used pure silicalite as well as silicalite modified by impregnation with various transition metals to convert methanol to isobutylene. At 345 – 450°C, 1 atm and 0.6 - 1.45 WHSV, selectivity to $C_2 - C_4$ olefins in excess of 70% was reported. Silicalite impregnated with molybdenum {59} was also found active in converting methanol to lower olefins.

Most of the other works done on silicalites pertained to diffusion {66,67}, adsorption {68}, and synthesis {64, 69-73}.

### *2.1.3 Methanol Conversion Over Wide Pore Zeolites*

Zeolites characterized by large pore (12-ring) openings such as mordenite, faujasites (X,Y) and ZSM-4 have been used to convert methanol to light olefins. Schwartz and Ciric {74}, were the earliest to investigate the methanol conversion reaction over wide pore zeolite catalysts. They reacted methanol over RE-X (rare-earth exchanged X-

type) and Zn-X (zinc exchanged X-type) zeolites. At 330 – 390°C, 1 atm and 1.5 LHSV, the gaseous products contained 43.3% and 34% $C_2 - C_4$ olefins for RE-X and Zn-X respectively. Methanol conversion was low and coke formation rapid.

Natural mordenite, exchanged with various cations, was found by Zatorski and Krzyzanowski {75} to be highly active for methanol conversion to low molecular weight hydrocarbons at 350 – 500°C, but to have short life-time. Synthetic mordenite in which part of the $Si^{4+}$ cations were isomorphously substituted by $B^{3+}$, $Ga^{3+}$, and $Fe^{3+}$, were investigated by Kljueva et al. {76}. They found the yield of olefin to decrease in the order BM > M > GaM > FeM (where M stands for mordenite). Methanol conversion over mordenite modified by 100% ionic-exchange with Be, Mg, Tl, Ce, Nd, Pb, Th, Nb and Rh was reported by Pop et al. {52}. Reaction was carried out at 400°C and the product distribution was largely determined by the type of cation. Some linearity correlations were found between Pauling electronegetivity of the metals used in the ion-exchange, and the amount of ethylene and propylene formed{52}.

Kubelkova et al. {77}, studied the methanol conversion over H-Y, AlH-Y and dealuminated Y zeolites. Under low pressure flow conditions (1 - 3 Pa) at 670K, the products of methanol transformation consisted mainly of lower olefins and aromatics. Mazzite or ZSM-4 {15}, H-L and NaH-Y {20}, were also found to convert methanol to olefins.

The major problem encountered in using this class of zeolites lies in the large cavities existing within the framework structure which permit formation of higher hydrocarbons and aromatics. In most cases, these cavities act as cages or 'traps' for the large molecules, leading to rapid coke formation and deactivation. Attempts have been made to reduce the coking tendency of the wide pore zeolites but most of these efforts had little success. Sawa et al. {78}, and Niwa et al. {79} reported developing a long-life dealuminated mordenite for methanol conversion to hydrocarbons. But their results also showed that while coke formation was suppressed due to change of acidity, large aromatics were also formed. The dealumination procedure similarly lead to slight narrowing of the pore openings.

### *2.1.4 Miscellaneous Catalysts Used In Methanol Conversion To Olefins*

Various metal salts of heteropolyacids have been found to catalyze the conversion of methanol to olefins. Heteropolyacids such as dodecatungstophosphoric acid ($H_3PW_{12}O_{40}$) and dodecatungstosilicic acid ($H_4SiW_{12}O_{40}$) were investigated by Baba et al.{80,81} and Hibi et al. {82}. Both teams of investigators obtained the corresponding metal phosphates and silicates by exchanging the acids with various cations. Selectivities to lower olefins was found to vary as a function of metal-loading and support type. Typical sequence of olefin selectivities for some exchanged acids was reported as {80}:

Al-TPA < Fe-TPA < Cu-TPA < Fe-TSiA < Cu-TSiA < Al-TSiA

where:

TPA = Tungstophosphoric Acid; TSiA = Tungstosilicic Acid

Kasai et al.{85}, investigated the synthesis of olefins from methanol over a variety of metal and organic salts of $H_3PW_{12}O_{40}$. The organic salts of phenazine, triethylenediamine and piperazine, did not exhibit selective formation of olefins. However, pyrazinium salts brought about remarkable improvement in the selectivity to ethylene and propylene. Silver salt of tungstosilicic acid ( $(Ag_4(SiW_{12}O_{40}))$ supported on Aerosil ($SiO_2$) was employed by Ehwald et al. {84} to synthesize olefins from methanol. Best results with respect to olefin production were obtained in the medium range of surface concentrations of the active component.

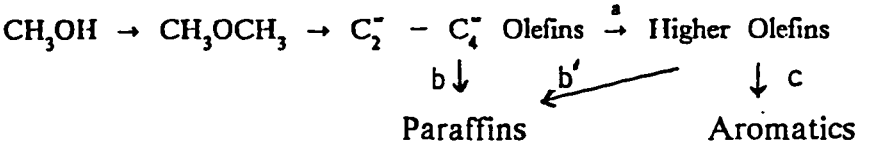
Clinoptilolite, a highly siliceous natural zeolite in its acidic form, was found active in converting methanol to light olefins {85}. Modification of the catalyst by treatment with mineral acids or ammonium salts gave product distribution which predominates in $C_2^-$ – $C_5^-$. Removal of Al by acids from the clinoptilolite framework lead to a decrease in selectivity for lower olefins whereas the deposition of sulphur on the surface, increased the selectivity up to 83% {86,87}. Hutchings et al. {87} however, observed that the clinoptilolite catalysts modified by either ammonium ion exchange or hydrochloric acid treatment, exhibited short active life (2-3hr) due to

high rate of coke deposition ($3.5x10^{-3}$ g carbon/g catalyst/h ) making them unsuitable for this reaction.

Fu-1, a new high silica zeolite, in its hydrogen form HFu-1 as well as in Ca- and RE-exchanged forms (CaFu-1, REFu-1), was found active in olefin formation from methanol {88}. Kikkawa et al. {89}, reported obtaining an olefin-rich product from methanol decomposition over aluminium dihydrogen phosphate $Al(H_2PO_4)_3$ supported on alumina-silica. At 375 - 425°C and 0.09 - 0.71 LHSV, $C_2 - C_4$ olefin selectivities of 20 - 60% were obtained. Zirconia ($ZrO_2$) treated with acid also converts methanol to olefins with high selectivity {90}.

## *2.2. Mechanisms of Methanol Conversion to Hydrocarbons*

Despite the voluminous amount of work done on methanol conversion to hydrocarbons, the mechanism by which the methanol molecule with one carbon atom gets transformed into the wide spectrum of product hydrocarbons, is still a subject of controversy. Different reaction schemes have been proposed involving intermediates such as carbenoids, oxonium ions, carbenes and free radicals. The overall reaction sequence of methanol conversion to hydrocarbons is however believed to be well represented by the following scheme {61}:




where:

Process a : $C_nH_{2n} \rightarrow C_mH_{2m}$ $(n=2,3,4,5), (m > 6)$

Process b, b′: $C_nH_{2n} \xrightarrow{+2H} C_nH_{2n+2}$ $(n > 2)$

Process c: $C_mH_{2m} \xrightarrow{-xH} C_mH_{2m-x}$ $(m > 6)$

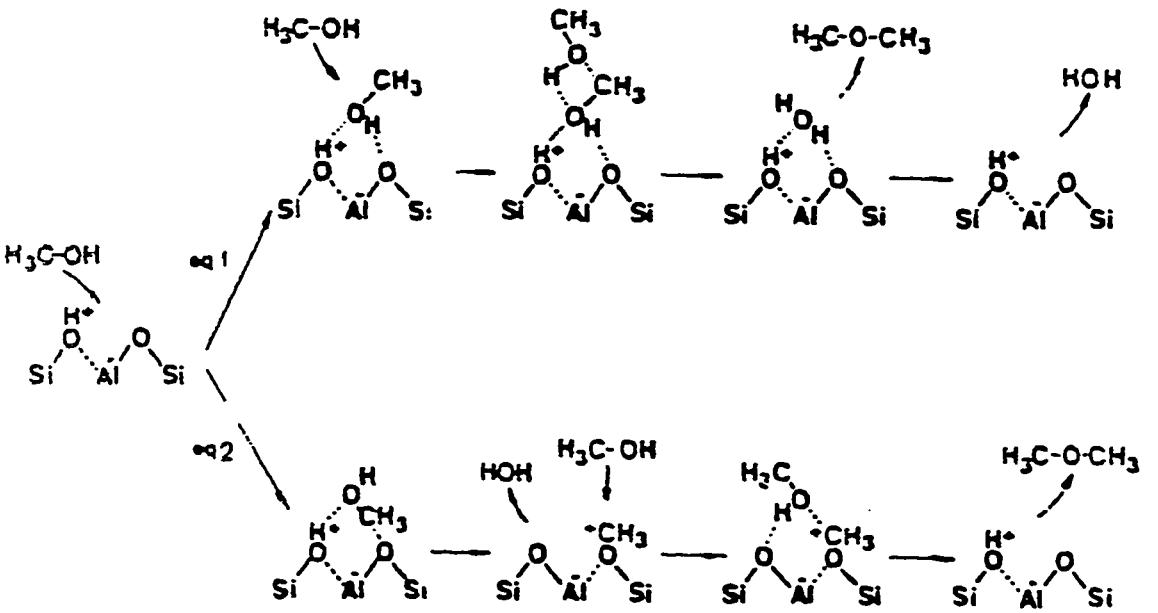
The mechanism of the reaction sequence is believed to involve three steps viz: a) ether formation, b) first C-C bond formation, and c) higher hydrocarbon formation.

### 2.2.1 Ether Formation

Methanol dehydration to dimethylether (DME) by acid catalyzed water subtraction is a well known reaction :

$$CH_3OH \xrightarrow[\text{Acidic Catalyst}]{-H_2O} CH_3\text{-}O\text{-}CH_3\ (DME)$$

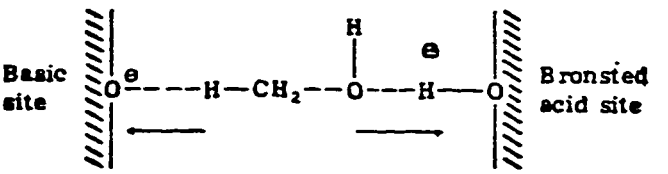
Van Hoof {91}, proposed the following mechanism for dimethylether formation over acidic sites in zeolites:



### 2.2.2 First C-C Bond Formation

The mechanism of initial C-C bond formation from methanol or DME has been subject to much controversy. Several postulations have been proposed but despite the abundant literature on the subject, unanimous agreement in support of any of these mechanisms is still lacking. Following, are some of the mechanisms proposed by various workers.

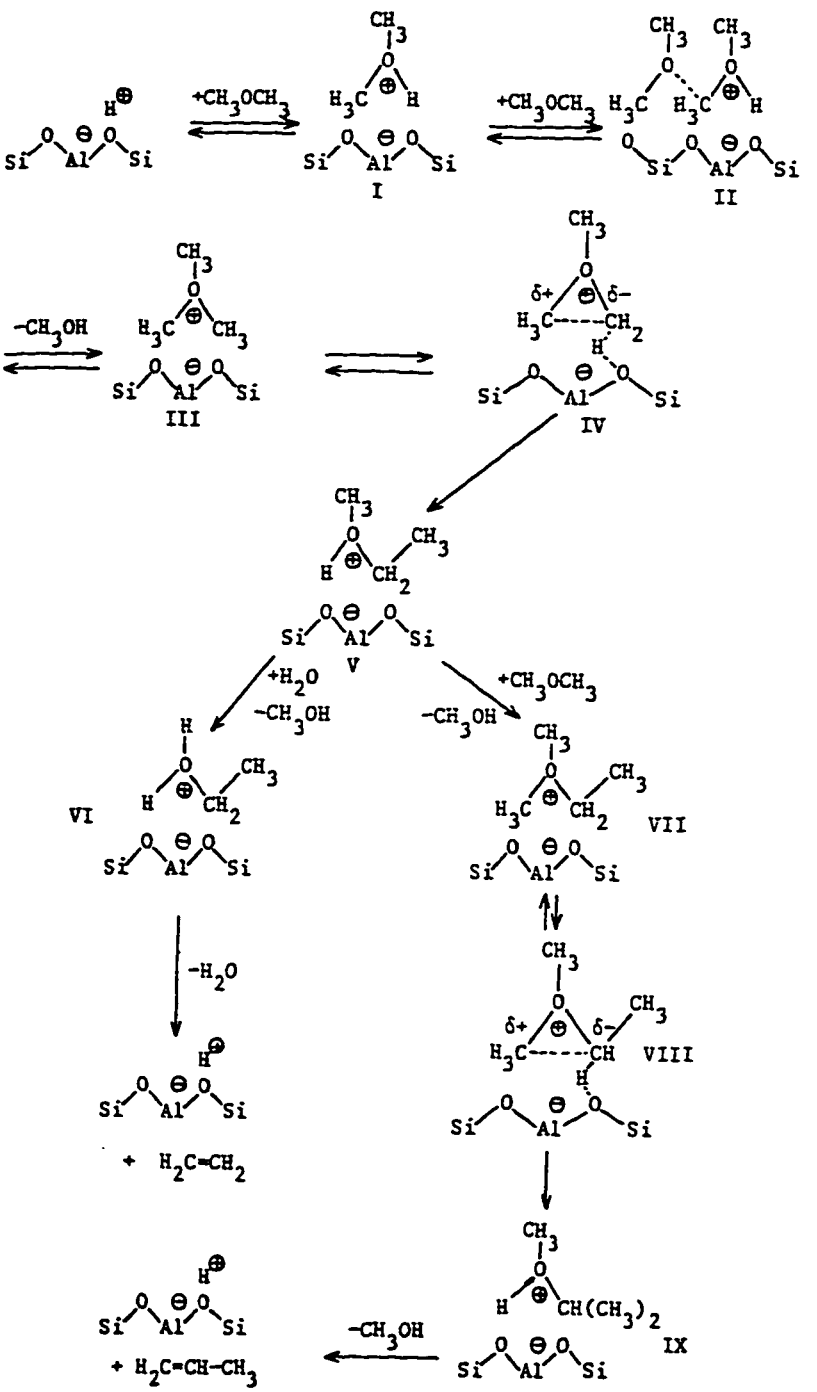
i. Carbene intermediacy{15,74}



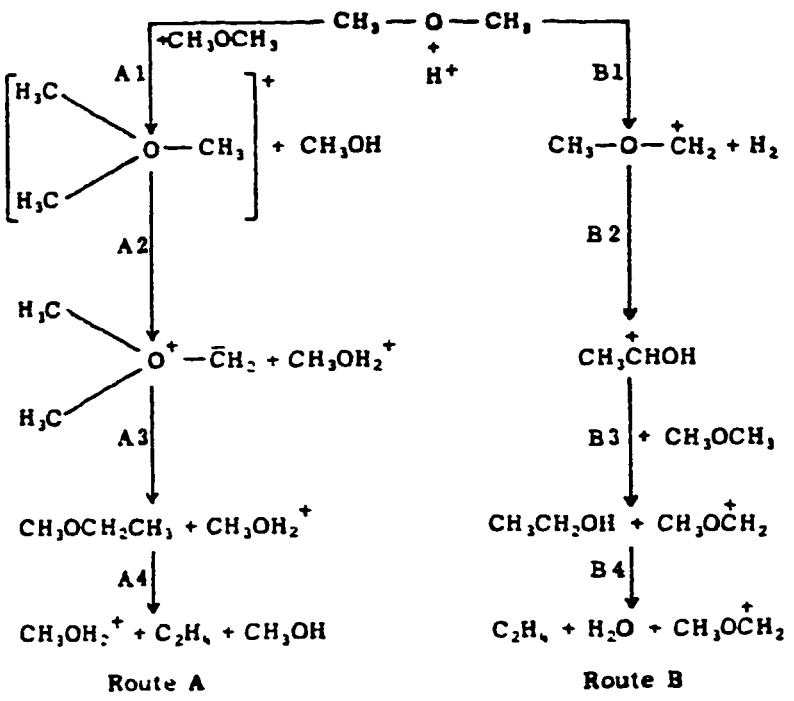

$$H{-}CH_2{-}\overset{\curvearrowright}{O}H \rightarrow H_2O + :CH_2$$

$$n{:}CH_2 \rightarrow (CH_2)_n, \quad n = 2, 3, 4, 5$$

ii. Oxonium ions and Ylids {93}



iii. Trialkyloxonium/Carboxonium Routes {92}



iv. Free Radical Mechanism {75}

$$CH_3OH \rightarrow \dot{C}H_3 + \dot{O}H$$

$$2\dot{C}H_3 \rightarrow C_2H_6$$

$$\dot{C}H_3 + C_2H_6 \rightarrow CH_4 + CH_3\dot{C}H_2$$

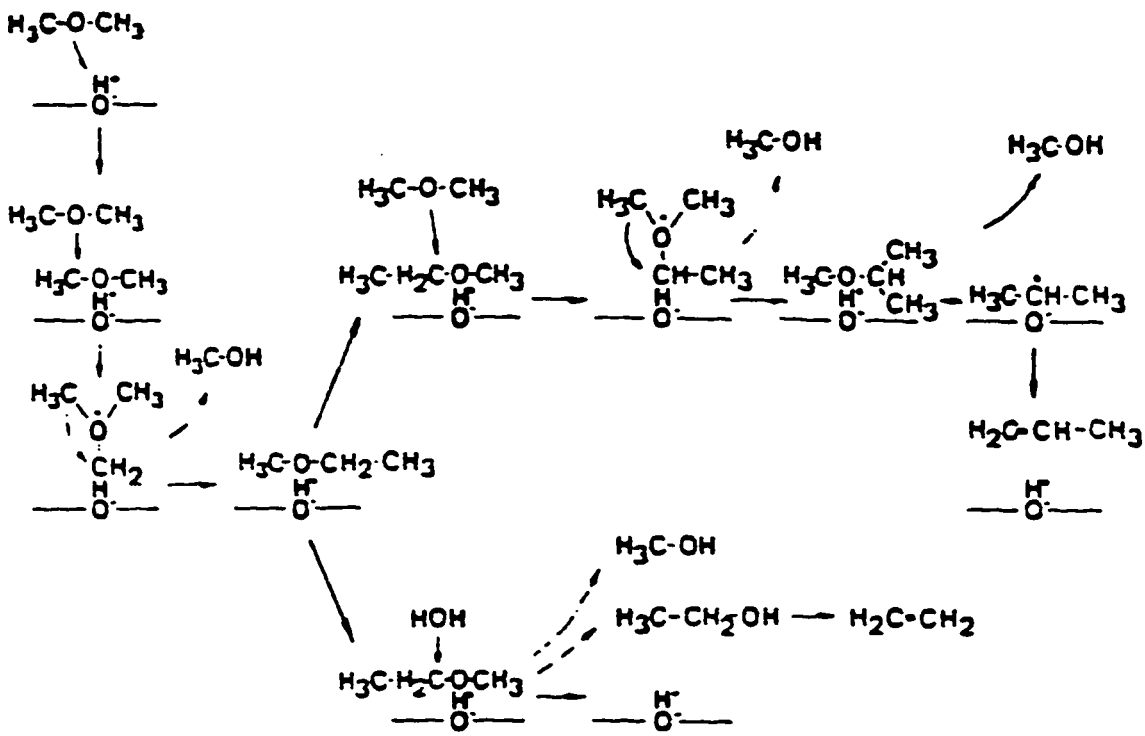
$$\dot{C}H_3 + CH_3\dot{C}H_2 \rightarrow C_3H_8$$

$$2CH_3\dot{C}H_2 \rightarrow C_4H_{10}$$

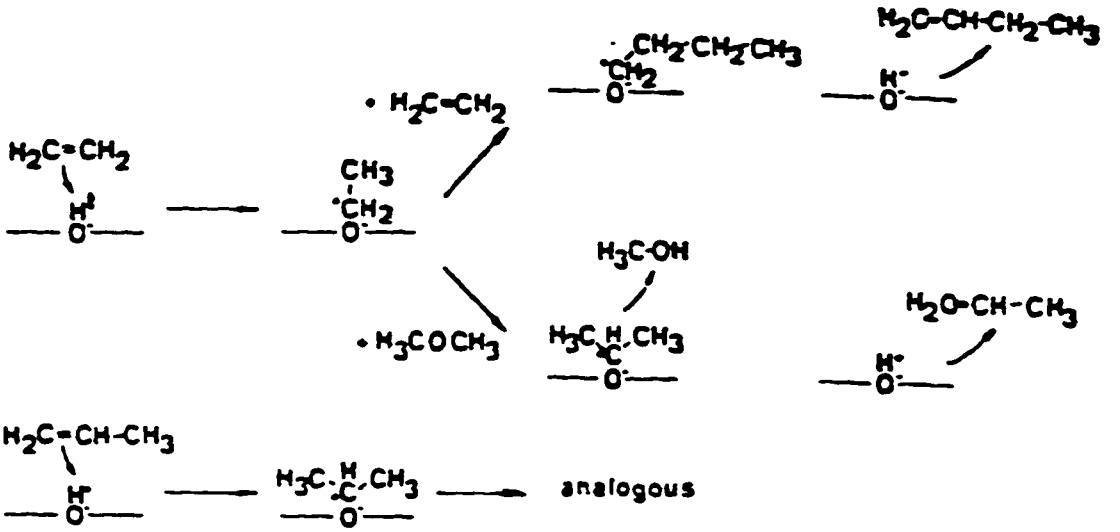
$$CH_3\dot{C}H_2 \rightarrow C_2H_4 + \dot{H}$$

### 2.2.3 Higher Hydrocarbon Formation.

Once the first C-C bond is formed, the reaction proceeds autocatalytically through chain propagation, oligomerization, homologation and cyclization reactions to produce higher aliphatics and aromatics. Van Hoof {91} proposed the following mechanisms for initial formation of ethylene and propylene and subsequent formation of higher olefins.



Formation of ethylene and propylene




Formation of higher olefins

Several other reaction mechanisms have been proposed on the mechanism of the methanol conversion reaction {15, 30, 38, 41, 42, 44, 94-96}.

## *2.3 REACTION KINETICS*

Light olefins are intermediates in methanol conversion to hydrocarbons over zeolite catalysts{13}:

$$\frac{n}{2}[\,2CH_3OH \rightarrow CH_3OCH_3 + H_2O\,] \rightarrow C_nH_{2n} \rightarrow n[CH_2]$$

where $[CH_2]$ = average formula of an aromatic-paraffin mixture.

Steps in this sequence are in general, kinetically coupled. The strong dependence of the product distribution on zeolite properties as well as reaction parameters coupled up with the autocatalytic nature of the reaction makes rigorous kinetic treatments of the reaction either impracticable or have little practical justification{15}. As discussed in the section on mechanisms, the overall reaction from methanol to olefins may involve as many as 27 reaction steps{95}. Very few researchers have thus worked towards developing kinetic models for the complex reaction mechanism. In this section, a brief review of works done on kinetic modelling of the reaction is presented.

Chen and Reagan {11} discovered that the methanol conversion reaction was autocatalytic. They proposed a model based on the following global scheme:

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} B$$

$$B \xrightarrow{k_3} C$$

where A = oxygenates, B = olefins, and C = aromatics + paraffins and $k_1$, $k_2$, and $k_3$ are rate constants. In order to optimize olefin formation, experiments were carried out at low conversion to make $k_3$ negligible. The following rate equation was used:

$$-\frac{dA}{dt} = k_1A + k_2AB$$

Integrating the above equation and rearranging variables in terms of $k_2$ gave the following expression:

$$k_2 = \frac{1}{(1 + R)t} \ln \frac{(R + B)A_o}{RA}$$

$$\text{Where } R = \frac{k_1}{k_2}$$

A good fit of the kinetic model to the rate data was obtained with $k_2 = 55$ and $k_1/k_2 = 0.02$, indicating that the initial rate of formation of ethylene from oxygenates is much slower than the rate of reaction of oxygenates with the product olefins. $k_2$ was also found to be linearly

dependent on the intrinsic acid activity of the catalyst {11}.

Autocatalysis was confirmed by Ono et al. {12}. However, a different kinetic model was proposed, involving a sequence of two bimolecular reactions:

$$A + A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} B$$

where A and B are oxygenates and olefins respectively. They assumed that the first reaction is second order with respect to the concentration of A, [A], and the second reaction being first order with respect to both [A] and the concentration of B, [B]. Letting x = conversion of A, $[A] = [A]_o(1-x)$, $[B] = [B]_o + [A]_o x$ and W = weight of catalyst, these result in:

$$\frac{1}{W}\frac{dx}{dt} = k_2 [A]_o (1-x) [(\alpha+\beta) + (1-\alpha)x]$$

where:

$$\alpha = \frac{k_1}{k_2} \text{ and } \beta = \frac{[B]_o}{[A]_o}$$

Integration of the above equation gave:

$$\ln\frac{\alpha+\beta+(1-\alpha)x}{\alpha+\beta)(1-x)} = k_2 W[A]_o(1+\beta)t$$

Reasonable fit was obtained and the activation energy for the rate constant $k_1$ and $k_2$ were estimated to be 1.6x $10^2$ kJ/mol and 1.1x $10^2$ kJ/mol respectively.

The scheme proposed by Chen and Reagan{11}, was modified by Chang {97} to incorporate a bimolecular term due to homologation of olefins:

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} C$$

$$B + C \xrightarrow{k_3} C$$

$$C \xrightarrow{k_4} D$$

where A = oxygenates, B = ($:CH_2$), C = olefins, and D = paraffins + aromatics.

The species B was assumed to have carbene-like character attacking both oxygenates and olefins. Invoking steady state assumption on B, and eliminating time, the following expression was obtained:

$$-\frac{du}{d\Lambda} = \frac{1}{\Lambda}\left[\left(\frac{1+K_1u}{2+K_1}\right)(1-K_2u) + u\right]$$

where u = C/A, $K_1 = k_3/k_2$, and $K_2 = k_4/k_1$. The equation was tested using data obtained on fixed bed microreactors at three pressures, and the parameters $K_1$ and $K_2$ were estimated using Marquardt algorithm.

Doelle et al. {98}, studied both sorption and reaction kinetics of methanol and dimethylether over ZSM-5. Analysis of data obtained at 115 – 200°C, showed that the reaction was found to obey:

$$r = \frac{k_1 P_{CH_3OH}}{1 + K_2 P_{H_2O}} \quad \text{with} \quad k_1 = 6x10^5 \exp\left[\frac{-80\ kJ/mol}{RT}\right] \frac{mol}{g.s.bar}$$

Mihail et al.{95}, developed a detailed kinetic model for methanol conversion to olefins over zeolites. They proposed a reaction mechanism consisting of 27 reaction steps. Rate equations were formulated and the different kinetic parameters were identified using Marquardt routine. Maria and Muntean{96} later simplified the reaction model proposed by Mihail et al.{95}. The simplification was achieved using discretization procedure combined with the integral procedure and ridge regression analysis. Rate expressions were formulated and the various parameters obtained using computer algorithms.

A global kinetic model for high temperature conversion of methanol to olefins was proposed by Chang et al.{13}, with the reaction scheme:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

where

A = oxygenates, B = olefins and C = aromatics + paraffins.

Both steps were assumed first order. Experimental data were fitted and rate constants determined. It was found that the temperature coefficient for olefin formation was much larger than that for aromatization and that the ratio $k_1/k_2$ (olefin/aromatic) increases with $SiO_2/Al_2O_3$ (silica/alumina) ratio of the zeolite catalyst.

It is clear from this review of the kinetic modelling of methanol conversion to olefins that a comprehensive kinetic model for the reaction is yet to be developed which can be used for process design. However, optimizing selective formation of light olefins, is believed to hinge on finding means to decouple the aromatization step. A number of approaches have been applied to limit the reaction sequence at the olefins stage{13}. These include a) shape selective catalysis, b) partial conversion with recycle, c) reaction at subatmospheric partial pressure, d) high temperature conversion, and e) modification of zeolite formulation. Several investigators have utilized one or more of these methods to optimize olefin contents of reaction products. Detailed treatments of their findings have been given in other sections (2.1.1 to 2.1.4).

## *2.4 FACTORS AFFECTING OLEFIN FORMATION*

### 2.4.1 Zeolite Properties

The distinguishing feature of zeolites is their well defined framework structures. Effects of zeolite pore size and channel structure on product distribution in methanol conversion reaction, has been discussed in section 2.1 and elsewhere {15,21,100}. Other important factors that affect the product spectrum include acidity and surface area.

The catalytic activity of zeolites is strongly related to acidity {100}. It is well known {61,38}, that in the H-ZSM-5 and related zeolites, Al is responsible for the formation of acid sites and their number increases with increasing Al content in the catalyst. The Bronsted acidity of a zeolites is thus commonly related with their $SiO_2/Al_2O_3$ ratio. Formation of lower olefins in methanol conversion was found to be favoured by high $SiO_2/Al_2O_3$ ratio since high acidity catalyzes the reaction towards higher hydrocarbons {101}. This was confirmed by Chang et al.{41}, and Balkrishnan et al. {59} who reacted methanol over ZSM-5 type zeolites with various $SiO_2/Al_2O_3$ ratios. As a typical example, by varying the $SiO_2/Al_2O_3$ ratio from 35 to 1280, Chang and co-workers increased the $C_2 - C_4$ olefins selectivity from less than 10% to about 80% {41}.

The role of acid sites in methanol conversion was investigated by Ono and Mori {12}. They exposed the catalyst to pyridine for 2h at 473K to neutralize strong acid sites. Using pyridine deactivated catalyst for

methanol conversion, the reaction product was dimethylether and no hydrocarbons were obtained. On the other hand, methanol conversion reaction over fresh catalyst at identical conditions gave about 85% total yield of hydrocarbons. This confirmed that acid sites were essential for hydrocarbon formation. The relationship between surface acidity and selectivity to $C_2 - C_4$ olefins was also studied by Balkrishnan et al. {59}. H-ZSM-5 with $SiO_2/Al_2O_3$ of 98, was treated by impregnation with Ni, B, and P to produce catalysts with different acid strengths. Acidity of the various catalysts was measured by the temperature-programmed-desorption (TPD) technique. The catalyst that exhibited highest selectivity for $C_2 - C_4$ olefins had the lowest concentration of strong acid sites. Conversely, the untreated H-ZSM-5 which had the largest concentration of strong acid sites, showed least selectivity to $C_2 - C_4$ olefins.

Surface area which is a function of crystallite size, has significant influence on the catalytic activity of zeolites. The effect of crystal size on the activity of ZSM-5 was investigated by Hermann et al. {102}. Methanol conversion was found to decrease from 75% to about 50 % as the crystal size was changed from 5um to 20um implying that not all the volume of the crystals was utilized.

### *2.4.2 Process Conditions*

Reaction parameters such as temperature, pressure and space velocity are important factors that influence olefin formation in the methanol

conversion reaction.

Chang and Silvestri{9} studied the effect of temperature and space velocity on product distribution in methanol conversion to hydrocarbons over zeolite catalysts. They carried out experiments at moderately low space velocities (LHSV 0.6 - 0.7) between 260 - 538°C. At about 260°C, the main reaction was the dehydration of methanol to DME and the hydrocarbons formed were predominantly $C_2 - C_4$ olefins. As the temperature increased to 340 - 375°C, the products contained substantial amounts of aromatics. With further increase in temperature to about 500°C, the light olefin content began to rise as a result of cracking reactions of aromatics and higher aliphatics. A similar trend was observed as the space velocity was varied at constant temperature, between 1 - 1080 LHSV ($h^{-1}$). At the lowest contact time (LHSV = 1080) corresponding with the least conversion, the product was mainly DME and the hydrocarbons formed contained about 78% $C_2 - C_4$ olefins.

Hoeldrich et al. {62}, investigated the influence of temperature on methanol conversion to lower olefins over aluminosilicate and borosilicate zeolites. They found that with aluminosilicates, a high $C_2 - C_3$ olefin yield could be affected at either a low temperature of about 300°C, or a high temperature of about 500°C. In contrast, the borosilicate zeolite exhibited high selectivity with respect to lower olefins only at about 550°C.

The effect of temperature on the selectivity of ZSM-5 zeolite was also reported by Zatorski et al. {103} and Chang et al. {41}. Both groups of workers observed that the optimum temperature for lower olefin selectivity was directly related to the space velocity. At moderate space velocities (1 - 8 $hr^{-1}$), high yields of olefins were obtained between 460 and 500°C.

Reactant partial pressure has significant effect on selectivity in hydrocarbon formation from methanol {104}. The effect of varying pressure, is mainly to change the selective rates of dehydration and aromatization steps in the reaction sequence. By lowering partial pressure, aromatization may be decoupled from olefin formation {13}. Increasing pressure, enhances the overlap of the two reactions leading to increased selectivity to polymethylbenzenes. In a study on the effect of pressure on product distribution in methanol conversion reaction, Chang et al. {104} reported that the selectivity of $C_2 - C_4$ olefins increased from 10.6 to 80.6% as the methanol partial pressure was lowered from atmospheric pressure to 0.07 atm. Among the drawbacks to this approach however, is the necessity for product recovery from dilute streams.

### *2.4.3 Feed Properties*

The nature of the product distribution in the methanol conversion reaction, is also influenced by feed properties. The type and amount of diluent used as well as the kind of carrier gas co-fed with feed mixture might exert a certain degree of influence on product selectivity and

distribution.

Hunter and coworkers {105}, studied methanol conversion to hydrocarbons over H-ZSM-5 zeolite catalyst in the presence of oxygen and nitric oxide using argon as carrier gas. The diluent gases were fed in concentrations of 1 and 3 mol%. They found that with nitric oxide, addition of 1 mol% had no effect either on catalyst activity or on product spectrum while 3 mol% only slightly enhanced catalyst deactivation. Conversely, addition of oxygen at these concentrations caused immediate and irreversible deactivation of the zeolite catalyst. Inui et al. {106} also investigated methanol conversion to hydrocarbons over H-ZSM-5 at low temperatures ( < 260°C ), in the presence of low concentrations of olefins and/or other alcohols. They reported that the conversion reaction was considerably accelerated by addition of 1% ethylene and propylene leading to an increase in gasoline selectivity. Addition of ethanol in 0.03% on the other hand increased the selectivity of $C_2$ to $C_4$ olefins from 20.7 to 25.6% whereas addition of the same amounts of isopropanal and allyl alcohol reduced the selectivity of $C_2$ to $C_4$ olefins from 20.7% to 16.3% and 17.1% respectively.

The effect of feed dilution with $H_2O$, $O_2$, $H_2$, CO,$CO_2$, and He on light olefin formation over H-ZSM-5 zeolite, was reported by Cichowlas et al. {107}. They contacted methanol with the various diluents at 460°C, $WHSV_{MeOH} = 10hr^{-1}$ and $p_{MeOH} = 0.015 - 0.025$ mPa. Among the different diluents, only water was found to exert a promoting effect on

prolonged activity of the catalyst. Zatorski et al. {58} and Gabelica {108} also confirmed that light olefin selectivity is enhanced by methanol dilution with water. Although water is a byproduct in the conversion reaction, addition of water in the feed causes both a decrease of the surface concentration of reaction intermediates and the shortening of contact time. Coke deposition is also suppressed resulting in prolonged catalyst lifetime. The major shortcoming of water dilution however, is the long-term dealumination of the zeolite leading to permanent deactivation and possible structural collapse of the zeolite framework.

# CHAPTER 3 : APPARATUS AND PROCEDURE

## *3.1 EXPERIMENTAL SET-UP*

The process diagram of the experimental set up is shown in Figure 3.1 . The apparatus consisted of four parts: feed section, preheating zone, reaction system and product separation section. Experiments were carried out at atmospheric pressure in a fixed bed tubular stainless steel reactor shown in Figure 3.2. The range of other reaction parameters and operating conditions are given in Table 3.1.

### *3.1.1 Feed Section*

The feed section was designed to supply the feed to the reaction system under controlled pressure and flow rate. It consisted of methanol storage tank, methanol feed pump, air and nitrogen cylinders, and a Brook's mass flowmeter. The feed tank (manufactured by Technical Services Division of KFUPM Research Institute), was equipped with pressure indicators, filling port and a side teflon tube to show the liquid level inside the tank. Methanol liquid stored in the vessel, was fed to the unit by a Milton Roy Minipump (Model 396-57). Nitrogen gas from a cylinder, was supplied at a regulated flowrate using Brooks mass flowmeter (Model 5850C) and mixed with the methanol before the preheating zone. Air , also stored in a cylinder, was fed during in situ

**TABLE 3.1 : Design Basis of the Experimental Setup**

| PARAMETER | DESIGN BASIS (UNITS) |
|---|---|
| Methanol Feed rate | 1 - 250 (ml/hr) |
| Nitrogen Flowrate | 0 - 1000 (cc/min) |
| Air Flowrate | 0 - 1000 (cc/min) |
| Preheating Temperature | 300 ($^{o}$C) |
| Furnace Temperature | up to 750 ($^{o}$C) |
| Pressure | 1 - 10 (atm) |
| Space Velocity WHSV | 1 -20 (hr -1) |

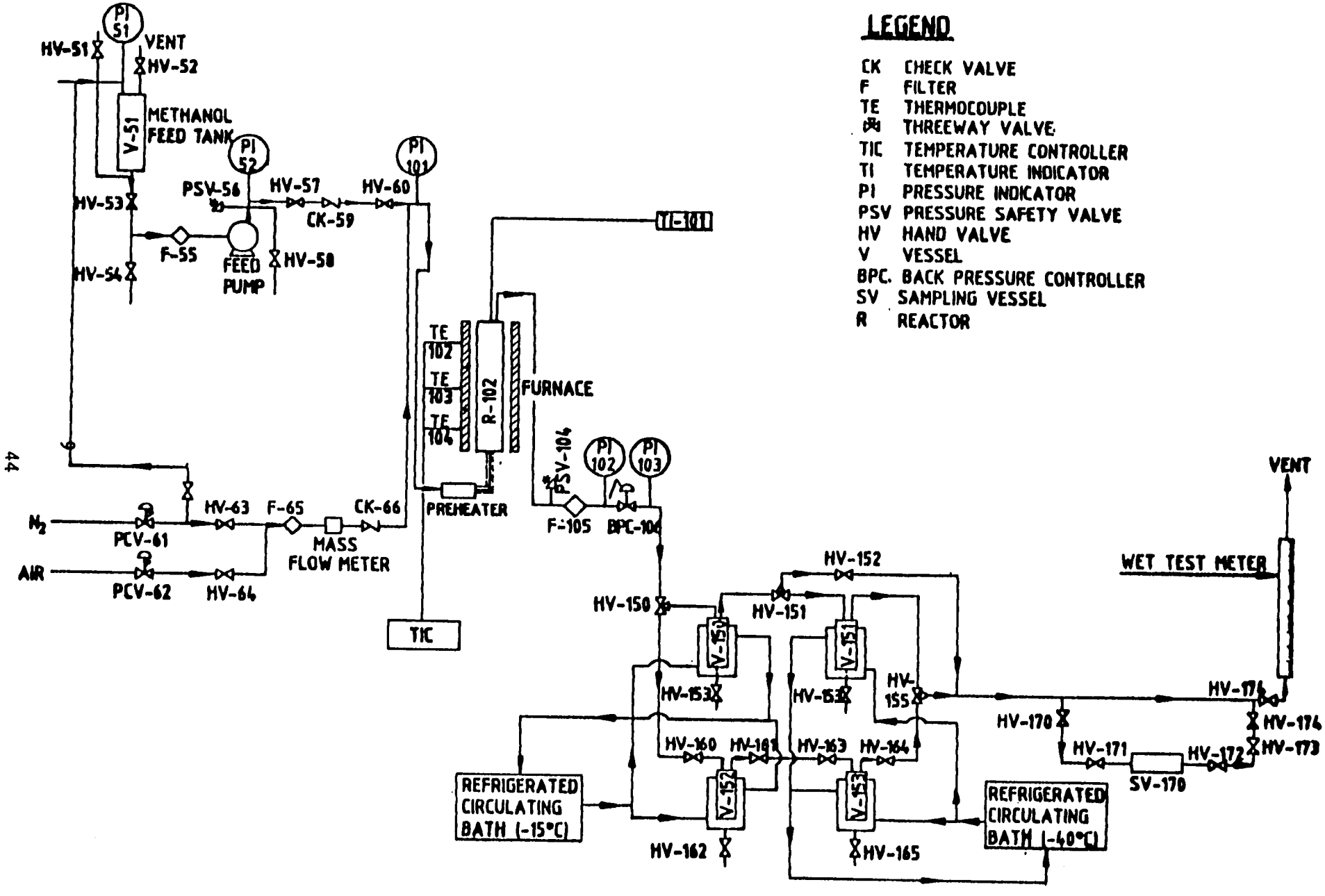



Figure 3.1. : Process Diagram For MTO Unit.

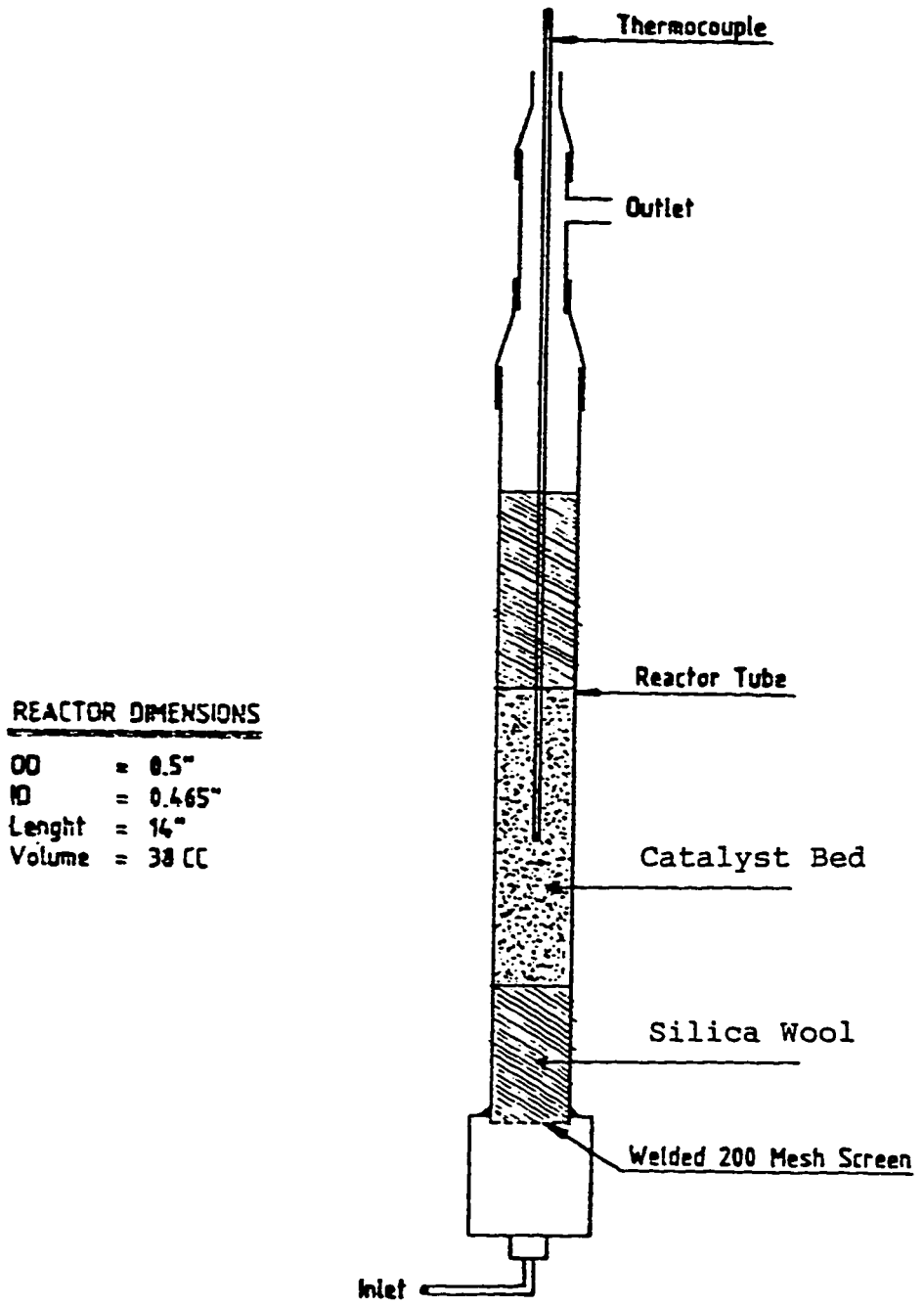



**Figure 3.2. :** Schematic Of The Reactor.

calcination and regeneration of catalyst. The various feeds were delivered to the reaction system through gas lines constructed of 1/4" stainless steel tubing.

### *3.1.2 Preheating Zone*

The methanol/nitrogen mixture was fed to the preheating section in which the methanol was vaporized to provide a homogeneous blend. The preheater was made of 2.5" o.d. stainless steel flash jacket insulated with a high heat-resistant tape to minimize heat loss to the surroundings and to maintain stable temperature during operation. The preheater temperature was measured using a thermocouple and controlled using an ON/OFF Omega controller.

### *3.1.3 Reactor Section*

The reactor used was a 38cc tubular stainless steel 0.5" O.D. tube. The catalyst sample was placed in the reactor and held in position using silica wool supports to provide a fixed bed operation. The temperature of the reactor was measured using a thermocouple located at the catalyst bed centre and controlled using a three-zone electric furnace (Thermcraft Inc. USA). The reactor is fitted with a mesh screen at the inlet, to distribute the feed mixture uniformly across the reactor radius.

### *3.1.4 Product Separation Section*

This section was designed to separate the reaction products into liquid and gaseous fractions. It consisted of a two-stage cooling system comprising two refrigeration circulators supplied by Brinkman Instrument Co. USA (Models RSM-6 and Model RKT-20). The units have capacities of 6 and 18 litres and operating ranges of -15°C to +120°C and -40°C to +20°C respectively. A mixture of ethylene glycol and water was used as the circulating medium. Condensed products are taken at sampling times through down flow drain valves located at the bottoms of the coolers. Gaseous products were led through rubber tubing, to glass sampling tubes.

## *3.2 EXPERIMENTAL PROCEDURE*

The procedure followed in carrying out experimental runs is summerized in Table 3.2. The following paragraphs give a brief description of the various steps

### *3.2.1 Reactor Packing*

Prior to loading the catalyst into the reactor, its bulk density was determined using a 5 cc graduated cylinder. From the reactor dimensions and weight of catalyst sample the length of the catalyst bed was calculated. This was done so as to position the reactor bed in such a way as to locate the thermocouple at the centre of the catalyst bed. Silica wool support was then placed into the reactor followed by the catalyst sample (5g) and topped by another amount of silica wool (Figure 3.2). The packed reactor was mounted in position on the reaction unit (inside the three-zone electric furnace) and pressure tested to ensure that the unit was leak-free.

### *3.2.2 Catalyst Calcination.*

The Catalyst sample was calcined in situ at 550°C for two hours under air stream flowing at 100cc/min. The purpose was to purge off water of crystallization and other impurities and volatile substances lying within the zeolite pores and cavities. The calcination involved stagewise heating of the sample according to the program shown in Table 3.3. Following the calcination at 550°C, the catalyst bed was purged with nitrogen gas for two hours at

**TABLE 3.2 : EXPERIMENTAL PROCEDURE**

| STEP | ACTIVITY |
|---|---|
| 1. | **REACTOR PACKING** |
| | - zeolite sample loading (5 gm) |
| | - pressure test |
| 2. | **CATALYST CALCINATION** |
| | - At 550 °C under 100cc/min air stream for 2 hrs. |
| | - Purging at 400 °C under 100cc/min nitrogen stream for 2 hrs |
| 3. | **RUN START** |
| | - reactor and preheater heat-up |
| | - product coolers start-up |
| | - methanol and nitrogen feed |
| 4. | **SAMPLING** |
| | - gaseous product sampling and injection into GCs |
| | - liquid product sampling and separation |
| 5. | **RUN STOP AND SHUTDOWN** |
| | - run stop at appearance of Dimethylether |
| | - catalyst bed drying under nitrogen flow of 100cc/min at 150 °C for 4 hrs |
| | - shutdown and reactor unloading |
| | - spent catalyst sample analysis for coke deposition |

100cc/min and 400°C, to ensure that the catalyst bed was cleaned of residual calcination products and any impurities.

**Table 3.3** : : Insitu calcination program for catalyst samples.

| Temperature | Duration |
|---|---|
| 150 °C | 15 min |
| 300 °C | 15 min |
| 400 °C | 15 min |
| 550 °C | 2 hrs |
| 400 °C : $N_2$ purging for two hours at 100 cc/min | |

### *3.2.3 Run Start*

The experimental unit was prepared for a run by starting the various sections of the reaction set up. The preheater and product separators were started and allowed to reach the set temperature. Gas chromatographs used to analyze gaseous products were also started. The catalyst bed was heated to the desired temperature using the three-zone electric furnace enclosing the reactor. Since the methanol conversion reaction is exothermic, the reactor temperature was usually set to an initial value lower than the intended reaction temperature.

Nitrogen feed which was started following calcination, was adjusted to the predetermined flowrate to give the required methanol-to-nitrogen ratio. When the various sections of the reaction set-up were stabilized at the set values, the methanol pump was started. The different parts of the reaction unit were then closely monitored until methanol reached the catalyst bed and reaction started. This was signalled by a sudden rise in the reactor temperature and pressure. The start conditions which included reactor temperature and pressure, preheater temperature, nitrogen and methanol flowrates, methanol tank level , methanol-pump starting time and the reaction start time were all recorded. The gaseous product flowrate was measured using a water-displacement 1000 ml graduated cylinder by determining the volume of gas collected within a given time interval.

### *3.2.4 Sampling*

Product samples were taken at specified intervals. Gaseous product samples were taken in air-tight gas sampling cylinders and injected into gas chromatographs for analysis. Liquid samples were taken at the bottom of gas-liquid seperators, weighed and separated into aqueous and organic fractions for further analysis. At each sampling time, the following parameters were recorded: a) Sampling time, b) total run time (hr), c) gaseous product flowrate (l/hr), d) weight of liquid produced, e) reactor temperature, f) reactor pressure, g) methanol flowrate (g/hr) and h) any peculiar observations or remarks.

### *3.2.5 Run stop and shutdown*

The experimental run and product sampling was continued until Dimethylether (DME) appears in the gaseous sample. This was noted as a DME peak in the chromatographic analysis. The presence of DME in the product mixture was taken as an indication of catalyst deactivation since DME is the precursor to olefins in the conversion reaction sequence. Before terminating the run however, few more samples were usually taken to observe the deactivation trend of the catalyst.

The methanol feed was then stopped but nitrogen flow was maintained at 100cc/min and reactor temperature at 150°C for about 2 - 3 hours to purge off unreacted methanol in the gas lines and reactor bed. The reactor was then cooled, dismantled and unloaded and the spent catalyst subsequently analyzed for coke deposition, surface area and pore size distribution.

## *3.3 CATALYSTS AND MATERIALS USED*

The various catalysts used in this study, are listed in Table 3.4 along with the names of the suppliers. The zeolite samples were selected and ordered following extensive literature search and were chosen among the zeolite types proven to be active for converting methanol to olefins. The objective was to screen the various catalyst formulations using the bench scale reaction unit in order to identify and select the most potential zeolite for further investigation.

The methanol utilized was Fluka-AG chemical grade (99.5% purity). Table 3.5 gives the list of physical and thermodynamic properties of methanol which is the sole reactant in this study. Other gases used were nitrogen, as carrier gas, and air which was utilized for in situ calcination and regeneration.

**TABLE 3.4 : List of Zeolite Samples and Suppliers**

| SUPPLIER CODE | TYPE | SUPPLIER |
|---|---|---|
| H-ZSM-5 | H-ZSM-5 | MOBIL |
| MZ-25 | ZSM-5 | |
| MZ-26 | X-Zeolite (rare earth exchanged) | |
| MZ-27 | Y-Zeolite (Ultra stable | |
| SAPO-34 | Silicoaluminophosphate | UNION CARBIDE |
| M-5 | Mordenite | |
| Y-52 | Y-Zeolite | |
| S-115 | Silicalite | |
| CREY | Y-zeolite | GRACE |
| USY | Y-zeolite(Ultra stable) | |
| HY | Y-zeolite (H-exchanged) | CROSSFIELDS |
| Zeolon 900 | Mordenite (H-exchanged) | PQ Corp. |

**TABLE 3-5 :** Physical and Thermodynamic Properties of $CH_3OH$ {1}

| Property | Value |
|---|---|
| freezing point, °C | −97.68 |
| boiling point, °C | 64.70 |
| critical temperature, °C | 239.43 |
| critical pressure, kPa[a] | 8096 |
| critical volume, mL/mol | 118 |
| critical compressibility factor $z$ in $PV = znRT$ | 0.224 |
| heat of formation (liquid) at 25°C, kJ/mol[b] | −239.03 |
| free energy of formation (liquid) at 25°C, kJ/mol[b] | −166.81 |
| heat of fusion, J/g[b] | 103 |
| heat of vaporization at boiling point, J/g[b] | 1129 |
| heat of combustion at 25°C, J/g[b] | 22,662 |
| flammable limits in air | |
| lower, vol % | 6.0 |
| upper, vol % | 36 |
| autoignition temperature, °C | 470 |
| flash point, closed cup, °C | 12 |
| surface tension, mN/m (= dyn/cm) | 22.6 |
| specific heat | |
| of vapor at 25°C, J/(g-K)[b] | 1.370 |
| of liquid at 25°C, J/(g-K)[b] | 2.533 |
| vapor pressure at 25°C, kPa[a] | 16.96 |
| solubility in water | miscible |
| density at 25°C, g/cm$^3$ | 0.78663 |
| refractive index, $n_D^{20}$ | 1.3284 |
| viscosity of liquid at 25°C, mPa-s (= cP) | 0.541 |
| dielectric constant at 25°C | 32.7 |
| thermal conductivity at 25°C, W/(m-K) | 0.202 |

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert J to cal, divide by 4.184.

## *3.4 CATALYST CHARACTERIZATION METHODS*

The performance of any zeolite in the methanol conversion reaction, depends on its physical, chemical, thermal and structural properties. In order to correlate the results obtained for an individual zeolite to its properties, a clear understanding of such properties is essential. The various zeolites were therefore fully characterized for chemical composition, surface area, pore volume, pore-size distribution, thermal stability, crystallinity and particle surface morphology. The results of three selected catalysts are reported in Appendix A. The different characterization techniques are summarized in Table 3.6 and described briefly in the following paragraphs.

### 3.4.1 Chemical Analysis

The chemical composition of a zeolite catalyst has significant effect on the nature and type of products formed over the zeolite catalyst. Common zeolite properties such as silica/alumina ratio, exchangeable cations and promoter-loadings are all determined from the chemical analysis. An accurate analysis of catalyst composition therefore helps to interpret its performance and optimize its utilization.

The instrument used for chemical analysis of both fresh and spent zeolite samples, was the Admiralty Research Laboratory (ARL) atomic emission spectroscope Model ARL-3580. The equipment uses the Inductively Coupled Plasma (ICP), which is an atomic emission spectroscopic technique where radio-

**TABLE 3.6 :** Characterization Methods and Equipments Used

| CHARACTERIZATION METHOD | PARAMETER MEASURED | EQUIPMENT USED |
|---|---|---|
| Chemical Analysis By Inductively-Coupled-Plasma (ICP)) | Elemental Composition | ARL-3580 (UK) |
| BET Method Nitrogen Adsorption/ Desorption | Surface Area | Sorptomatic-1800 + HEC 960 Micro-computer (Italy) |
| Pore Characterization by mercury penetration | Pore Volume and Pore Size Dist. | Porosimeter 2000 (Italy) |
| Thermal Analysis (TG, DTA) | Weight Loss, Endothermicity Exothermicity | Simultaneous Thermal Analyser STA-429 (W. Germany) |
| XRD | Crystallinity | Philips PW/170 X-Ray Diffractometer (Netherlands) |
| SEM | Surface Morphology | JEOL JSM-840 (Japan) |

frequency power is coupled to a specially designed quartz torch establishing the plasma in Argon. This high temperature plasma source, excites the species introduced and each element emits radiation of a particular wavelength. This emission intensity is measured by a spectrometer that facilitates the elemental determination at the trace level. The ICP model ARL-3580, was equipped with various channels that allow the simultaneous determination of 48 elements shown in Table A-1 in Appendix A. However, with the exception of Al, Si, Na, P, Ca, Fe, Sr, Te and Ti , all other elements were found in quantities less than 0.1%. Results of chemical analysis for three selected zeolites are given in Table A-2 in Appendix A.

### 3.4.2 Surface Area

The surface area of a catalyst has pronounced effect on the amount of gas adsorbed and on its activity as a catalyst. Hence for catalytic reactions over zeolites, the area (expressed in $m^2/g$), gives a measure of the zeolite surface available for chemical reactions. The most common method applied in determining the total surface area of catalysts, is that developed by Brunauer, Emmet, and Teller (called the BET method). In this technique, the amount of nitrogen adsorbed at equilibrium at its normal boiling point (-195.8°C) is measured over a range of partial pressures below 1 atm. The Langmuir adsorption isotherm is then extended to apply to multilayer adsorption arriving at the following equation{109}:

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{(c-1)p}{cv_m p_o}$$

where

$p$ = partial pressure (mm)

$v$ = volume of nitrogen adsorbed at pressure p($cm^3$ at STP)

$v_m$ = volume of monolayer gas ($cm^3$ at STP)

$p_o$ = vapor pressure (mm)

$c$ = constant for the particular temperature and gas-solid system

A plot of $p/v(p_o-p)$ versus $p/p_o$ gives a straight line, which can be extrapolated to $p/p_o = 0$. From the intercept (I) and the slope (S) of the plot, the volume of adsorbed gas corresponding to a monolayer can be obtained using the relation:

$$v_m = \frac{1}{(I + S)}$$

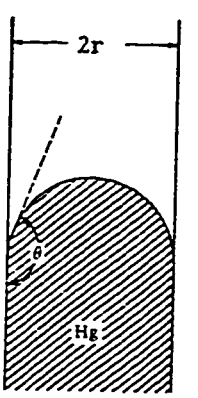
Volume $v_m$ can be readily converted to the number of molecules adsorbed and hence to the surface area of the solid adsorbent. Typical results of three selected zeolites are given in Table A-3 in Appendix A.

### 3.4.3 Pore Volume and Pore-size Distribution

Catalyst pores are generally visualized to be an array of randomly oriented cylindrical capillaries of different shapes, sizes and lengths. The characteristics

of zeolite pores play important role in determining individual zeolite shape selectivity since the pores act as channels through which reactants gain access to catalytic sites and products diffuse out from the framework structure. Knowledge of pore properties is therefore essential to gain an insight into the variety of catalytic reactions taking place within the zeolite framework structure.

One of the techniques applied in measuring the pore-size distribution in catalysts is by high pressure mercury penetration. The method is based on the fact that mercury has a significant surface tension and does not wet most catalyst surfaces. This means that the pressure required to force mercury into the cavities of a porous material depends on the pore sizes of the substance. At equilibrium, the external force applied on the mercury becomes equal to the force resisting entrance caused by the surface tension of mercury. For a cylindrical pore with given size, the pore radius is related to the applied pressure according to the following expression{109}:




$$r = \frac{-2\sigma\cos\theta}{p}$$

where

r = pore radius (A)

p = applied pressure ($lb/in^2$)

$\theta$ = contact angle between mercury and pore wall (deg)

$\sigma$ = surface tension of mercury (lb/in)

Hence the smallest pore size that can be detected by this method depends on the maximum pressure to which mercury can be subjected by a particular equipment.

The apparatus used for determining the pore volume and pore-size distribution of the zeolite samples was Porosimeter 2000 (Carlo Erba Strumentazione, Italy), which was controlled and monitored by an HEC 960 microcomputer. The maximum capacity of the porosimeter was 2000 bars, and under the operating conditions, the smallest pore size measurable by the apparatus was 37 Å. Pore volumes and pore-size distribution of some of the zeolite samples are given in Table A-3 in Appendix A.

### 3.4.4 Thermal Analysis

Catalytic reactions, such as methanol conversion to light olefins, are normally carried out at elevated temperatures. The zeolite over which the reactions take place should maintain thermal stability over the ranges of operating temperatures. Thermal analysis is therefore done to study the changes in the zeolite properties as it is subjected to a controlled temperature program. The techniques applied are of two types i) Thermogravimetry (TG) and ii) Differential Thermal Analysis (DTA). In thermogravimetry, the change in mass of the zeolite sample is measured as function of temperature. DTA on the other hand, is a means of determining the amount of heat evolved or absorbed by the material and the temperature at which such changes take place. The temperature difference between a substance and a reference material is measured as both the substance and the reference material are subjected to a controlled heating program. Among the phenomena that can be identified by these techniques are: dehydration, desorption, solid-state and solid-gas reactions, vaporization, fusion, phase transformation, and crystalline transition.

The apparatus used for thermal analysis of the zeolite samples was a Simultaneous Thermal Analyzer (STA-429) manufactured by Netzsch, W. Germany. The equipment performs both TG and DTA at the same time. In the thermograms, the weight loss, differential temperature and sample temperature are all plotted simultaneously. Results of thermal analysis for the three selected zeolites are given in Table A-4.

### 3.4.5 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD), is a technique to measure the degree of crystallinity of a substance. As already mentioned in previous sections, the important property of zeolites is their well defined crystalline structure. The various zeolites, being crystalline solids have characteristic X-Ray powder diffraction patterns which are used for their identification and provide an indication of its purity.

The equipment used to measure the crystalline pattern of the different zeolites was a Phillips PW/1730 X-Ray diffractometer. Typical results of three zeolites are given in Appendix A4.

### 3.4.6 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM), is used to identify the characteristics of single particles and for examining the topology of the catalyst surface. SEM produces clear images of specimens ranging from objects visible to the naked eye to structures as small as several nanometers. The importance of this technique lies in making possible, visual assessment of zeolite particles both before and after reactions. The SEM equipment used was JEOL JSM-840. Size or microstructure can be determined in the range of about 1 nanometer to 30 micrometers. Results of SEM for the selected zeolites are presented in Appendix A5.

## *3.5 MODIFICATION OF ZEOLITE SAMPLES*

Modification of catalyst formulation is affected through incorporation various elements into the framework structure. It is well known that addition of small quantities of specific modifiers to some catalysts bring about remarkable enhancement in their selectivities to certain reaction products {56,61}. Based on this background, researchers have worked towards improving the activity and selectivity of various zeolites through modifying the zeolite composition by introducing a variety of promoters into the zeolite framework. A number of methods have been applied to affect such modifications, the main ones being: i) impregnation, ii) ion-exchange, iii) physical blending, and iv) synthesis. Modification by physical blending did not appear to be effective since the basic intrinsic properties of the blended phases remain unaltered. Incorporation of promoters at synthesis stage was outside the scope of this study since the zeolites utilized were commercially prepared and supplied by the propriety producers. The techniques employed in modifying the zeolites under study were thus impregnation and ion-exchange.

### 3.5.1 Modification by Impregnation

The procedure for zeolite impregnation involved addition of nitrate solutions of the elements of interest to the zeolite powder to firstly make a slurry and then suspension. This was followed by vigorous stiring overnight. The mixture was then vaporized under vacuum, dried overnight at 110°C and calcined in air at

550°C for two hours. The $NO_3$ part of the metal salt got vaporized at the calcination stage leaving the desired element loaded onto the zeolite crystallites.

### 3.5.2 Modification by Ion-Exchange.

Modification by ion-exchange was also done using nitrates of the sought elements. In this procedure however, the zeolite powder was first calcined at 550°C for 1 hr, cooled to room temperature and then slowly wetted into slurry form. The slurry was then heated to 80°C by immersion into a water bath maintained at 80°C. 1N solution of the desired nitrate was prepared and also heated to 80°C using a round-bottomed flask. The zeolite slurry at 80°C was instantly added to the nitrate solution and the mixture stirred for one hour at 80°C. It was then cooled, centrifuged, washed with distilled water and dried at 110°C.

## *3.6 ANALYTICAL METHODS*

The MTO reaction products consisted of gaseous and liquid phases. The liquid phase usually comprised of two distinct organic and aqueous layers which were separated for analysis.

The gaseous products were analyzed using two Gas Chromatographs (GC) Hewlet Packard model HP-5880A and Perkin Elmer model 8700. The gaseous products consisted of complex mixture of hydrocarbons (such as paraffins, olefins and aromatics), oxygenates (e.g. dimethylether, methanol, water), and permanent gases like CO, $CO_2$, $O_2$, and $N_2$. Separation of complex mixtures such as these, required long high resolution capillary columns. Therefore, a 50m CP-Sil 5 column was employed in the Perkin Elmer 8700 GC. In the HP-5880A GC however, three separate columns were used for various components. A 29 ft Bis(- 2-methoxy ethyl) Adipate and DC 200 column was utilized to separate $C_6$, $C_5$, $C_4$ , and $C_3$ hydrocarbons. . In the second stage , 6 ft Porapak Q column separates $C_2$ 's and $CO_2$ while a 10 ft Molecular Sieve 13X was used at the third stage to separate CO, $CH_4$, $N_2$ and $O_2$. All columns in the 588A-HP GC were in 1/8 inch OD stainless steel. Due to lack of calibration standards however, not all the products could be quantified. In addition, the Flame Ionization Detector (FID) was limited to identifying combustible gases only and could thus not be used to detect permanent gases like $CO_2$, $O_2$, $H_2$, and $N_2$. Emphasis was therefore given to light olefins and alkanes which were the main products of interest under investigation.

The organic layer was separated from the aqueous layer and analyzed by PONA-Gas-Chromatography which gave qualitative analysis of Paraffins, Olefins, Naphthenes, and Aromatics. The aqueous portion of the liquid product which also contained unreacted methanol, was analyzed using Karlfisher titration. This method gave accurate quantitative analysis of water in a mixture. From the results of Karlfisher titration, the amount of unreacted methanol was determined, which was inturn used to calculate product yields and conversions.

The calculation procedure adopted in data analysis to determine conversions and component yields is given in Appendix C.

# CHAPTER 4 : RESULTS AND DISCUSSIONS

## *4.1 Preliminary Studies On Reproducibility And Screening Of Zeolite Samples for Methanol-to-Olefins Conversion*

Preliminary investigation was carried out to test the performance of the reaction system in terms of methanol conversion as well as reproducibility of experimental data. Screening studies were also conducted on six different zeolite samples to test their performance on the methanol conversion reaction to light olefins.

### 4.1.1. Reproducibility Studies

In order to establish the reliability of the reaction set-up, sampling and analytical procedures and to define confidence limit in the experimental data, reproducibility runs were carried out at 375 °C and 400 °C, using S-115 zeolite catalyst. Two runs were carried out at each temperature and adequate attention was given to ensure duplication of identical experimental conditions in each set so as to eliminate possible causes of deviation in the results. Results of overall evaluation of the runs in terms of conversion and product distribution, are given in Tables C-2 and C-3. A plot of yield of light olefins as a function of life-on-stream of the catalyst for the two sets of runs are given in Figures 4.1 and 4.2. The maximum absolute deviation observed in the light olefins yield was 9.7% at 400 °C and 12.3% for the data obtained at 375 °C. This sets a reasonable limit of confidence on collected data considering the multiple factors that might be sources of errors. These factors include temperature fluctuation (in preheater

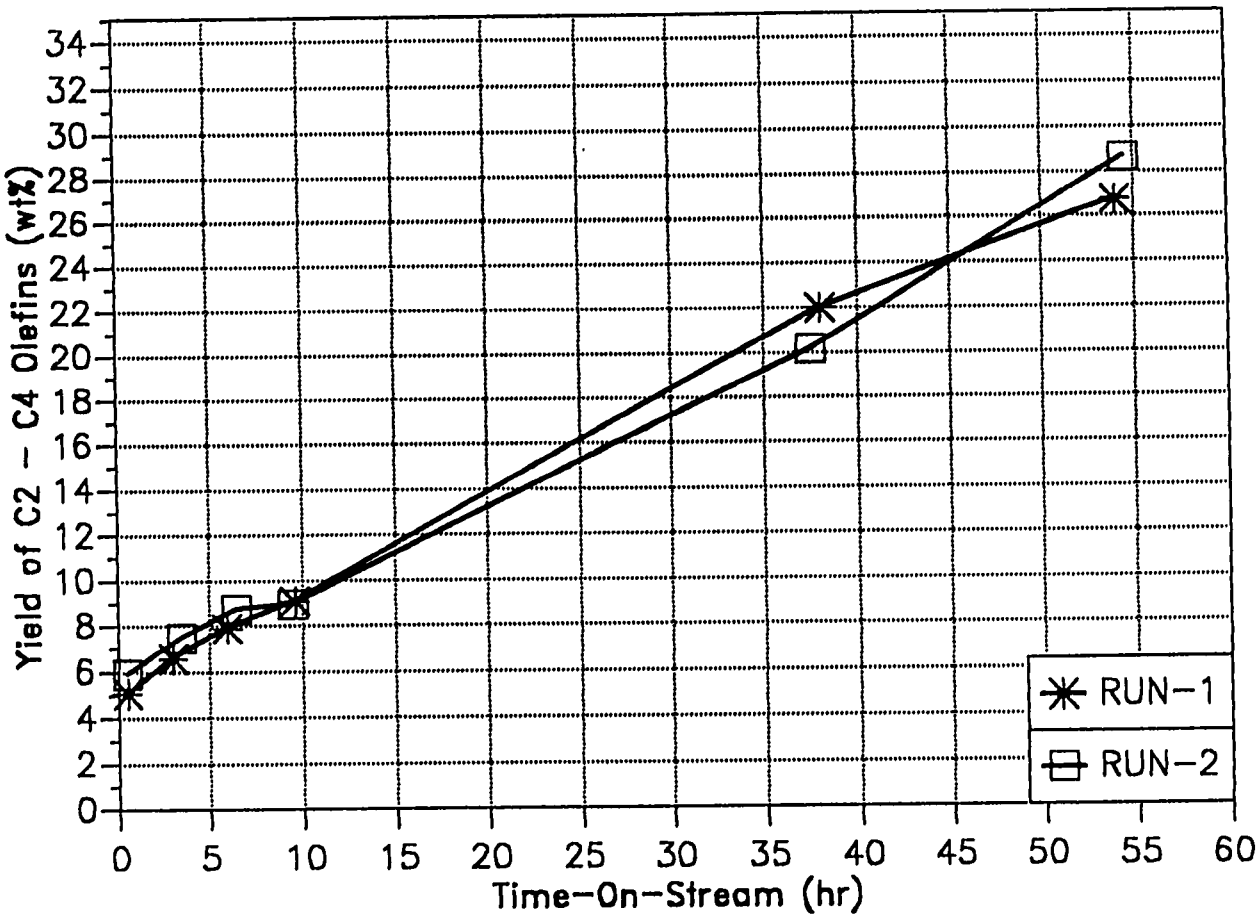



Figure 4.1 : Reproducibility Runs For Silicalite S-115 at 400°C, 4 $h^{-1}$ WHSV and 2.67 Methanol-to-Nitrogen (wt) Ratio

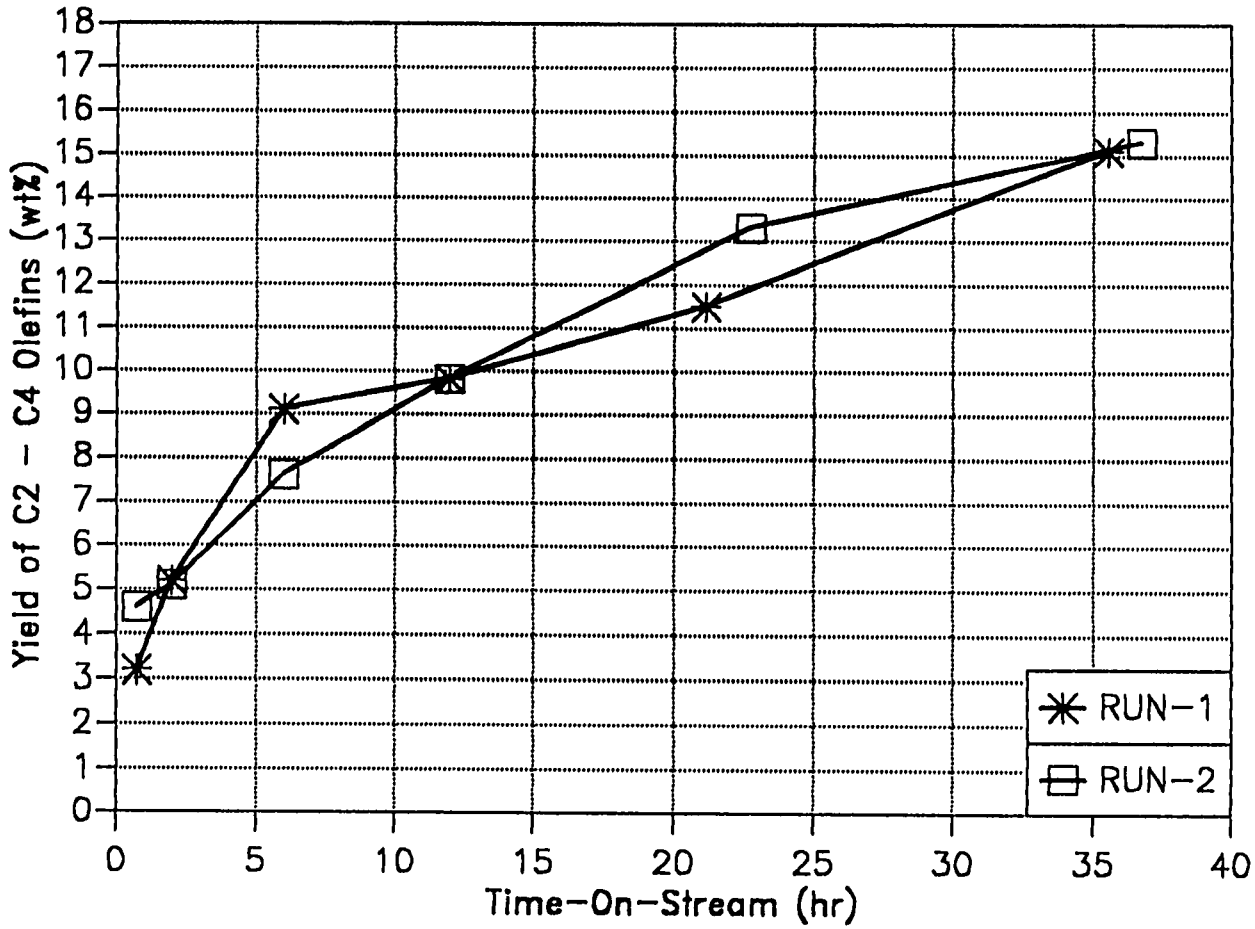



Figure 4.2 : Reproducibility Runs for Silicalite S-115 at 375 °C, 4 $h^{-1}$ WHSV and 2.67 Methanol-to-Nitrogen (wt) Ratio

and reactor), measurements of gas flow rates, catalyst bed packing, in-situ calcination of catalyst sample and inherent errors in analytical equipments (such as gas chromatographs), that give compositional analysis.

### *4.1.2 Screening Studies on Fresh Commercial Zeolites*

Six zeolite types namely SAPO-34, ZSM-5, S-115, RE-X, US-Y and MZ were selected for screening studies. Experiments were carried out at 400°C, 4 $hr^{-1}$ WHSV, and 1 atm. Other reaction parameters are shown in Table 4.1. The experimental conditions for the screening studies were chosen following literature search on previous works related to MTO conversion. Although the results of each study depend on the catalyst used, in general the methanol conversion reaction was found to be favoured under these conditions.

Characterization results of the various zeolites, established that they were thermally stable between 200 - 600°C (Appendix A3). The surface areas of the catalysts ranged between 180 - 600 $m^2/g$, $SiO_2/Al_2O_3$ ratio varied between 3 - 300 while pore volumes were found to be in the range of 0.48 to 1.73 cc/g. Results of the performance of the various zeolites are presented in Table 4.2. Product distributions for the different catalysts are illustrated in Figure 4.3 and the yields of total $C_2$ to $C_4$ olefins as a function of time-on-stream, are plotted in Figure 4.4.

**TABLE 4.1 :** Reaction Parameters For Screening Studies

| | | |
|---|---|---|
| Catalyst Weight | : | 5g |
| Methanol Flowrate | : | 20g/h |
| Nitrogen Flowrate | : | 100cc/min |
| Preheater Temperature | : | 180 °C |
| Reactor Temperature | : | 400 °C |
| Reactor Pressure | : | 1 atm |
| Cooler Temperature | : | 1 °C |

## SAPO-34

SAPO-34, which belong to the chabazite family of narrow pore zeolites, exhibited highest yield of light olefins ( 32.9%) but had short active life time of 0.8 hours. Rate of coke deposition was also high showing 6.4 wt%/hr. This phenomenon is typical of small pore zeolites. The chabazite framework structure, is known to posses ellipsoidal supercages of dimensions roughly 13 × 15 Å {15}. At molecular levels such dimensions are large enough to permit formation of aromatics as well as branched molecules with diameters larger than the zeolite channel sizes . These molecules cannot diffuse out and hence become trapped within the cell. Under reaction conditions such molecules get either cracked to smaller molecules or decomposed to carbonaceous compounds leading to blockade of active sites and deactivation. However, the observed high rate of coke deposition, coupled with the short life time of the catalyst seems to favour the latter phenomenon. This was further confirmed by the absence of any noticeable organic layer in the liquid product (Figure 4.3). Based on these results, it was concluded that SAPO-34 may not be suitable for fixed bed operation under the selected operating conditions in the reaction set-up used.

## ZSM-5 and S-115

ZSM-5 and silicalite S-115 belong to the medium pore pentasil type class of zeolites and are known to posses identical framework structure. Compared to SAPO-34, the two catalysts showed higher stability of activity and resistance

Table 4.2 : Results of Screening studies on various zeolite types at 400 °C, at 4hr $^{-1}$ WHSV, and 2.7 MeOH/Nitrogen (wt) ratio.

| PARAMETERS | ZEOLITE TYPE | | | | | |
|---|---|---|---|---|---|---|
| | ZSM-5 | SAPO-34 | S-115 | REX | USY | Mordenite |
| Total Life-on-stream (h) | 22.5 | 2.0 | 67 | 5.2 | 2.0 | 7.0 |
| Life up to DME(h) | 17.0 | 0.8 | 67 | 1.4 | 0.5 | 0.5 |
| Rate of Coke Dep. (wt%/h) | 0.6 | 6.4 | 0.1 | 2.9 | 9.4 | 1.2 |
| Average Conversion (%) | 89.1 | 93.5 | 92.3 | 90.1 | 90.1 | 61.5 |
| Water (g/100g MeOH)* | 41.0 | 13.0 | 51.1 | 30.6 | 27.8 | 34.1 |
| *Light Hydrocarbon Distribution (C-wt%)* | | | | | | |
| $C_2^=$ | 0.7 | 10.1 | 5.8 | 0.3 | 0.8 | 1.2 |
| $C_3^=$ | 0.7 | 14.7 | 14.4 | 0.2 | 0.5 | 0.68 |
| $C_4^=$ | 1.4 | 8.1 | 12.0 | 0.5 | 0.5 | 0.5 |
| Total $C_2^= - C_4^=$ Olefins | **2.8** | **32.9** | **32.2** | **1.0** | **1.8** | **2.3** |
| $C_1$ | 3.8 | 0.7 | 2.6 | 1.9 | 3.2 | 1.0 |
| $C_2$ | 1.1 | 1.1 | 0.6 | 0.2 | 0.5 | 0.2 |
| $C_3$ | 17.0 | 11.1 | 5.9 | 0.5 | 2.0 | 1.4 |
| $C_4$ | 17.5 | 2.8 | 9.6 | 0.6 | 2.4 | 1.0 |
| $C_5$ | 6.9 | 0.6 | 6.6 | 0.2 | 1.6 | 2.1 |
| Total $C_1 - C_5$ Alkanes | **46.3** | **16.3** | **25.3** | **3.4** | **9.7** | **5.7** |
| *Product Distribution (C-wt%)* | | | | | | |
| Gaseous Hydrocarbons | 49.1 | 49.2 | 57.5 | 4.4 | 11.5 | 8.0 |
| Organic Liquids | 34.6 | 0 | 25.4 | 0 | 0 | 0 |
| Others** | 16.3 | 50.8 | 17.1 | 95.6 | 88.5 | 92.0 |

* Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether

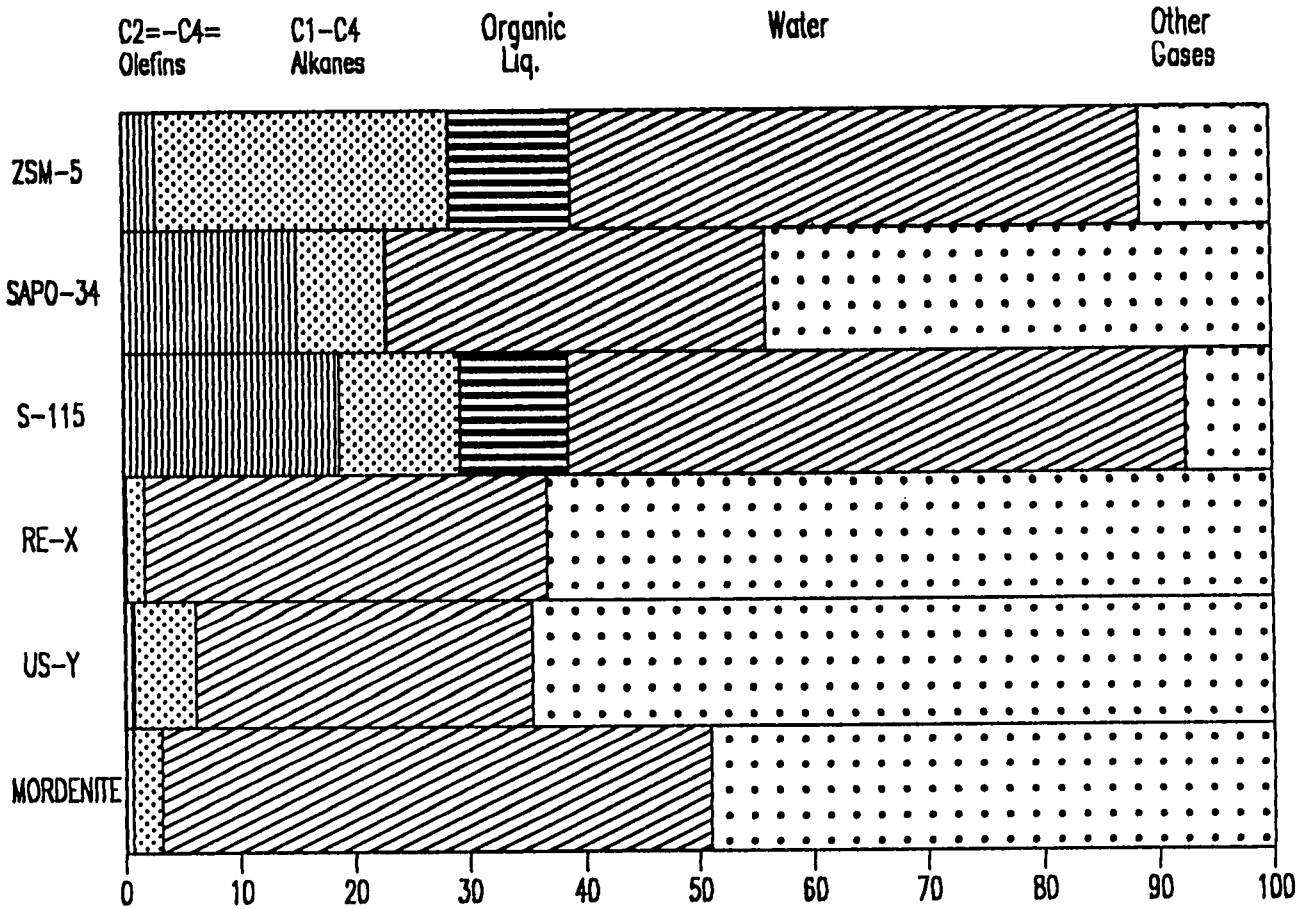



Figure 4.3 : Product Distribution for Screening Studies of Various Zeolites at 400°C, 4 $hr^{-1}$ WHSV and 2.7 Methanol/nitrogen (wt) ratio

to coke deposition. ZSM-5 had an active life time of 17 hrs with overall total olefin yield of 2.8 % (Table 4.2). It was however more selective to saturated hydrocarbons giving $C_1$ to $C_5$ total alkane yield of 46.3 % . The alkane fraction consisted mainly of propane and butane. S-115 exhibited better olefin selectivity and had longer active life-on-stream than ZSM-5. Combined $C_2$ to $C_4$ olefin yield (carbon wt%) totalled 32.2 % while $C_1$ - $C_5$ alkane yields was recorded as 25.3 % . The catalyst lasted for 67 hours before dimethyl ether appearance signalling deactivation. Rate of coke deposition observed was 0.6 and 0.1 wt%/hr for ZSM-5 and S-115 respectively.

Since the two catalysts have similar framework structure, one factor that accounts for the disparity in the product distribution of the zeolites could be the difference in their silica/alumina ratio. ZSM-5 had a silica/alumina ratio of 48.5 as compared to S-115 which had a silica/alumina ratio of 300. The Bronsted acidity of a zeolite is strongly associated with its alumina content. A zeolite with low silica/alumina ratio (in other words high aluminium content) would thus posses ample acidic sites to catalyze the reaction towards saturated hydrocarbons. Chemical analysis of the zeolites, showed that although the Si content of the two catalysts was approximately the same, the elemental Al in ZSM-5 was recorded as 1.67 wt% which was approximately 6 times the Al content in S-115. This explains the higher acidity of ZSM-5 which lead to higher yields of $C_1$ to $C_5$ alkanes of 46.3 % in contrast to S-115 which had a yield of the same components as 25.3 %. Another reason that could account for the variation in product distributions for the two zeolites is the difference in the residence times of reactants in the catalyst bed. ZSM-5 had a pore volume

approximately twice that of S-115 (1.7 and 0.8 cc/g respectively) giving the reaction mixture relatively longer contact time in ZSM-5 than in the case of S-115. This would have permitted the reaction to proceed further towards completion forming more saturated hydrocarbons. In S-115 on the other hand, the shorter residence time curtails the reaction sequence at the intermediate species leading to preponderance of olefins in the product mixture.

The presence of other elements as impurities within the zeolites's lattice structure might have influenced the performance of the individual catalysts as well. Results of the chemical analysis showed that ZSM-5 contained elements such as calcium (Ca) and titanium (Ti) in quantities exceeding 1800 ppm whereas S-115 had the same elements but in amounts less than 350ppm (Table A-2 in Appendices). It has been observed previously, that product distribution over zeolites might be influenced by presence of metal cations even at small concentrations (eg Si/Metal ratio of 3200) {56,61}. Small quantities of Ca and Ti incorporated into ZSM-5 has been found to effect the reaction products {52,58}. Their presence in the zeolite samples under investigations is expected to affect the product components. However, although the precise nature of the influence exerted by such elements on the reaction is not clear, the contrasting results exhibited by the two zeolites suggests sufficient evidence to attribute the nature of products obtained, to the disparity in quantities of these elements within the zeolites frameworks. The higher rate of coke deposition in ZSM-5 as compared to S-115, might also be related in a way to the presence of such elements.

**RE-X, US-Y and Zeolon-900 Mordenite**

Other zeolites included in the screening studies were RE-X (rare earth exchanged X zeolite), US-Y (ultrastable Y Zeolite), and Mordenite (Zeolon-900). These catalysts have framework structures characterized by wide pore (12-ring) channel system. The silica-to-alumina ratio of these zeolites ranged from 3 to 11 - indicating high aluminium content - while pore volume ranged between 0.5 and 1.1 cc/g. These zeolites exhibited poor activity, short active life-on-stream and generally, high rates of coke deposition. Yields of lower olefins varied between 1.0 and 2.3% while active life time was in the range 0.5 to 1.4 hours. The rate of carbon formation recorded ranged between 1.2 and 9.4 wt%/hr.

Large pore zeolites such as X and Y are normally designed for cracking processes conducted in fluidized bed operations{110}. Such zeolites formed for commercial usage, are in most cases strongly acidic and thus ultimately protonic. In the case of the zeolites under investigation, their high aluminium contents coupled with the wide pore structure and presence of large cavities, probably explains why the catalysts did not promote the methanol conversion reaction.

While studying acidity of mordenite zeolites, Kuhl {111} encountered difficulty in converting a commercial hydrogen mordenite to its sodium form. Subsequent investigation led him to conclude that commercial hydrogen mordenites ( or at least the two samples studied by him) may not always be true hydrogen zeolites. These findings might suggest a similar situation being encountered in the zeolite sample under investigation. Hence the zeolite types under study do not appear suitable as they are, for the methanol conversion reaction. This was further confirmed from the plot of total yields of light olefins

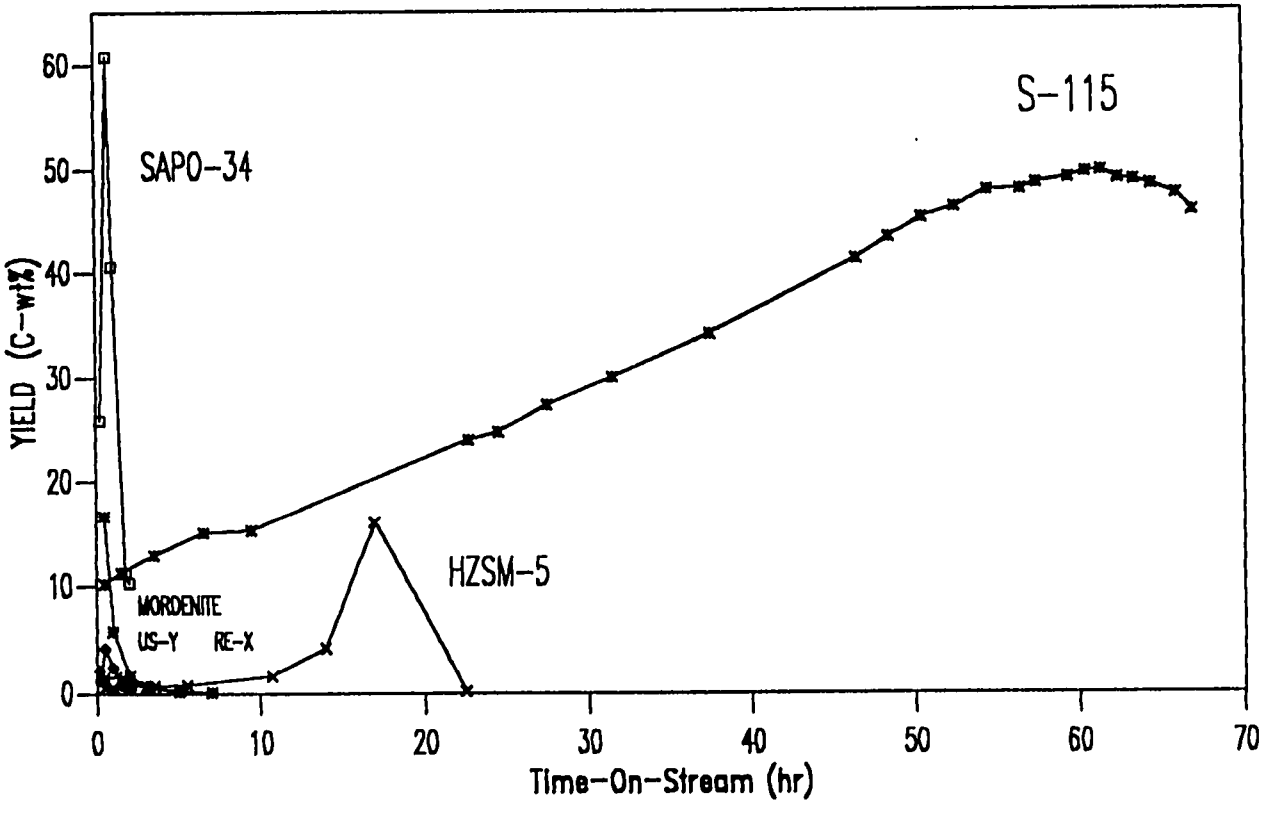



Figure 4.4 : Total Olefin Yields Versus Time-on-Stream for Various Zeolites at 400°C, 4 $hr^{-1}$ WHSV and 2.7 MeOH/N (wt/wt) ratio

versus time-on-stream depicted in Figure 4.4. Nonetheless, if modified by suitable promoters or applied at operating conditions different from the ones used in this study, it is likely that the zeolites exhibit a completely different activity performance.

**Selection of Catalyst For Further Investigation**

The criteria for judging the suitability of a catalyst for a specific reaction are numerous and in most cases depend on the particular process to be accomplished. In general however, a good catalyst should posses high stability under operating conditions, high activity and selectivity to desired products and low rates of coke deposition. Based on these criteria and the screening results of the six zeolite types presented in Table 4.1 and illustrated in Figures 4.3 and 4.4, ZSM-5 and S-115 proved to be the more potential zeolites for converting methanol to olefins in terms of activity, selectivity and coke formation. Although SAPO-34 showed high selectivity to light olefins, its high rate of coke deposition and short active life-on-stream (0.8h) makes it unsuitable for the conversion reaction under the operating conditions in the reaction set-up used. The olefin yield for ZSM-5 was expected to be improved through additional investigation which included parametric optimization as well as modification with various elements. S-115 and ZSM-5 were therefore selected for further study.

## 4.2 *Studies on Modified ZSM-5 and Silicalite S-115 Zeolites*

Various promoters were incorporated into the structures of the selected zeolites using the impregnation method described in section 3.5.1 . The modified versions of the catalysts were tested in the reaction unit to evaluate the effect of the individual promoters on the performance of individual zeolites. Each of the modified catalyst was also characterized for chemical, thermal, SEM and XRD analysis as well as surface area, pore volume and pore-size distribution. Results of the chemical analysis confirmed that the various modifiers have been loaded onto the zeolites . This was further established by the slight reduction in surface areas of the modified catalysts compared to the fresh zeolites. The thermograms and SEM photographs of the modified catalysts showed close resemblance to the fresh zeolites ascertaining that the thermal and structural properties of the zeolites were not altered by the impregnation procedure.

### 4.2.1 ZSM-5 Modifications

ZSM-5 zeolite was impregnated with Indium (In), Silver (Ag), Copper (Cu) and Cadmium (Cd). No previous work was reported on modification of ZSM-5 by impregnation with these elements (Appendix C). Results of the activity tests carried out at 450°C are given in Table 4.3 and Figure 4.5. The results of unmodified ZSM-5 are also included for comparison.

Table 4.3 : Effect of Promoters on the Performance of ZSM-5 at 450 °C, 4 $hr^{-1}$ WHSV, and 2.7 methanol-to-nitrogen (wt) ratio

| PARAMETERS | Promoter (2.5% Impregnation) | | | | |
|---|---|---|---|---|---|
| | - | In | Ag | Cu | Cd |
| **Total Life-on-stream (h)** | 25.5 | 2.0 | 10.25 | 8.75 | 2.0 |
| **Life up to DME(h)** | 24 | 1.0 | 9.25 | 7.25 | 1.0 |
| **Coke Dep. Rate (wt%/h)** | 0.6 | 3.2 | 1.3 | 1.5 | 4.2 |
| **Average Conversion (%)** | 90.1 | 87.0 | 88.0 | 90.9 | 79.1 |
| ***Light Hydrocarbon Distribution (C-wt%)*** | | | | | |
| $C_2^-$ | 2.7 | 5.2 | 3.3 | 2.9 | 1.7 |
| $C_3^-$ | 4.5 | 5.6 | 4.5 | 3.3 | 0.8 |
| $C_4^-$ | 2.7 | 4.2 | 2.4 | 2.2 | 0.2 |
| **Total $C_2^- - C_4^-$ Olefins** | **9.9** | **15.0** | **10.2** | **8.4** | **2.4** |
| $C_1$ | 3.8 | 9.2 | 8.4 | 9.0 | 11.0 |
| $C_2$ | 1.3 | 0.4 | 1.4 | 1.4 | 1.2 |
| $C_3$ | 15.4 | 3.0 | 15.3 | 13.3 | 0.5 |
| $C_4$ | 17.8 | 4.2 | 13.2 | 10.7 | 0.5 |
| $C_5$ | 8.7 | 3.0 | 5.3 | 4.4 | 0.4 |
| **Total $C_1 - C_5$ Alkanes** | **47.0** | **19.8** | **43.6** | **38.8** | **17.2** |
| **$C_2 - C_4$ Olefin Selectivity(%)*** | **10.9** | **33.1** | **11.9** | **10.5** | **9.4** |
| ***Product Distribution (C-wt%)*** | | | | | |
| **Gaseous Hydrocarbons** | 56.9 | 34.8 | 53.8 | 47.2 | 19.9 |
| **Organic Liquids** | 33.7 | 10.5 | 31.6 | 32.9 | 5.7 |
| **Others**** | 9.4 | 54.7 | 14.6 | 19.9 | 74.4 |
| **Water (g/100g MeOH)***** | 45.5 | 28.4 | 41.1 | 46.9 | 28.4 |

* Selectivity = (Olefins/Total Hydrocarbons)x100
** include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether
*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

### *Product Distribution*

Impregnation of the zeolite with various promoters brought about notable change in the product distribution. The yields of olefins of the modified catalysts was found to decrease in the order In > Ag > Cu > Cd. In-modified catalyst, gave total olefin yield of 15% as compared to the unmodified zeolite which had a yield of 9.9 %. This represented a 56% increase in the total olefin yield. Ag showed only marginal improvement whereas Cu and Cd gave lower olefin yields than the unmodified ZSM-5 catalyst (Table 4.3).

The yields of $C_1$ - $C_5$ alkanes and organic liquids for the modified catalysts were generally less than the fresh zeolite. Ag and Cu showed slight reduction in the amounts of alkanes whereas In and Cd decreased the alkane yields drastically from 47% down to 19.8 and 17.2 % respectively. It was interesting however to note that despite of the variation in yields of gaseous hydrocarbons, the different modified catalysts, maintained relatively the same olefin/alkane ratio as the fresh zeolite. Yields of organic liquids were also reduced slightly by modification with Ag and Cu but was severely decreased by addition of In and Cd.

### *Life-on-stream Performance*

The yields of total $C_2$ - $C_4$ olefins as a function of time-on-stream for the various modifications are presented in Figure 4.5.. With the exception of Cd, all other promoters increased the olefin yields within the initial few hours of reaction. Considering the yield of olefins for the fresh zeolites at times-on-stream equivalent to total active life time of individual modified catalysts, In, Ag, and Cu showed relative improvement of 330%, 113%, and 79% respectively. The olefin yields for Cd-modified however showed a decrease of about -23% even by this comparison. The curves of olefin yield versus time-on-stream for the various modifications, showed striking similarity in pattern (Figure 4.5). For each of the zeolites, olefin yields increased steadily as a function of reaction time until a peak was reached before a sudden sharp fall in the yields of olefins. The maximum points usually corresponded with the appearance of dimethylether which for the ZSM-5 catalyst, was mostly symptomatic of terminal deactivation.

### *Coke Deposition*

Modification of the zeolite with various promoters brought about increased rates of coke deposition. The rates of carbon formation for the impregnated zeolites ranged between 1.3 and 4.2 wt%/h as compared to the unmodified zeolite which had coke deposition rate of 0.6 wt%/h. The increase in rates of carbon formation in the modified zeolites can be attributed to the incorporation of the modifiers within inter-crystalline sites of the zeolite. Clusters of promoter atoms might be deposited in the vicinity of pore entrances or at locations within

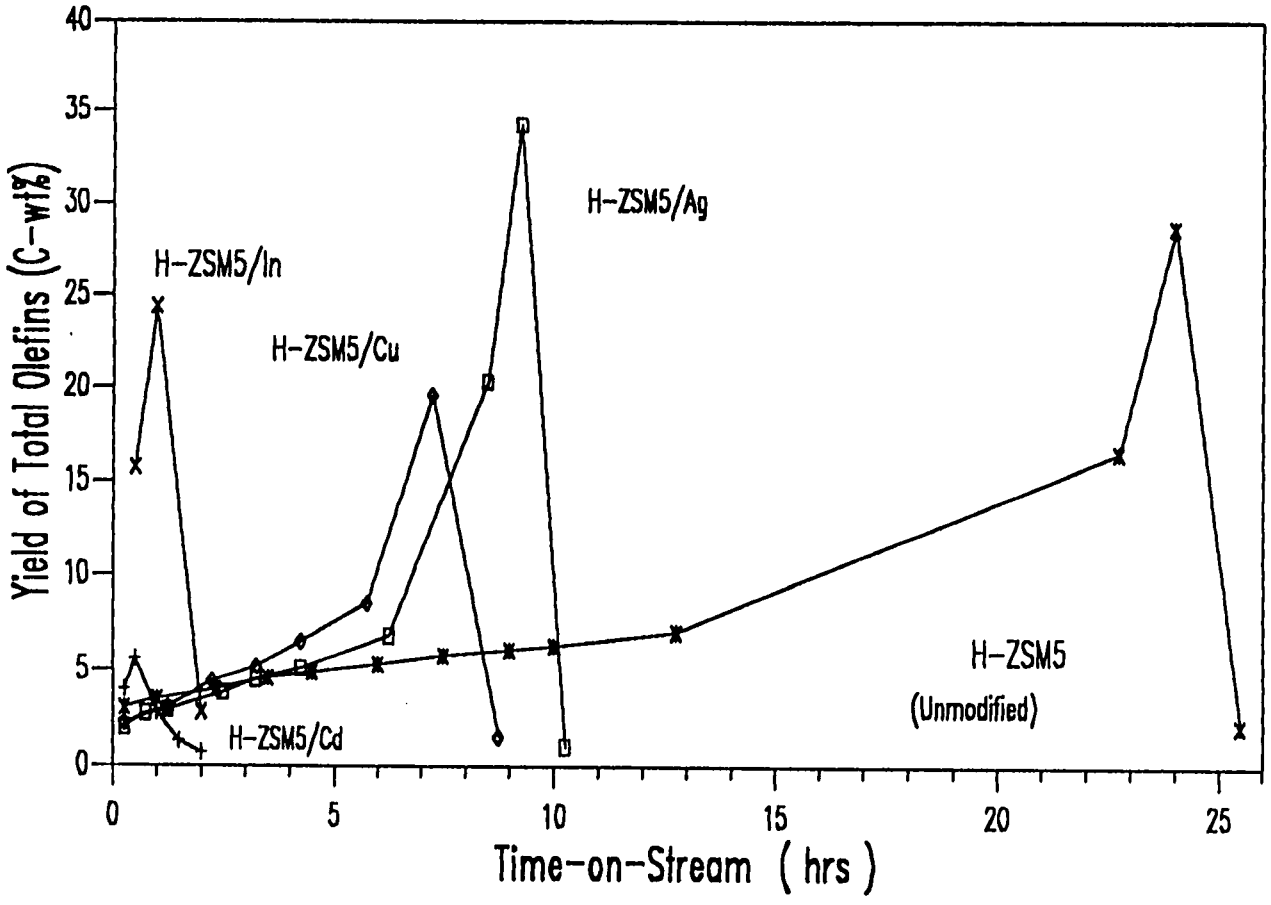



Figure 4.5 : Total Olefin Yields Versus Time-on-Stream for Various Modifications of ZSM-5 Zeolite at 450°C and 4 $hr^{-1}$ WHSV

macropores that are wide enough to contain such impregnated particulates. This would have lead to diffusional constraints for both reactants and products resulting in early decomposition of products with concomitant coke lay down. The promoter atoms could also occupy acidic sites of the zeolite leading to poisoning of active catalytic centers. They can also enhance the lewis acidity of the zeolite leading to accelerated coking. The sharp reduction in the active life time of the modified catalysts is indicative of such poisoning, possibly aggravated by the reversible poisoning resulting from coke deposition.

### 4.2.2. Silicalite S-115 Modifications

Relatively less work has been published on methanol conversion to olefins over modified silicalite catalysts. Therefore Calcium (Ca), Copper (Cu), Gallium (Ga), Strontium (Sr), Silver (Ag), Cadmium (Cd), Indium (In), Barium (Ba), and Lanthanum (La) were selected for modification of the commercial S-115 zeolite. The impregnation was carried out using nitrates of the various elements.

Results of the performance of the various modified zeolites are given in Table 4.4. while the product distributions for each of the modified catalysts are illustrated in Figure 4.6. Also included are the results of unmodified S-115 for comparison.

***Product Distribution***

The product spectrum of the modified zeolites varied according to the type of promoter incorporated. Total yields of $C_2^-$ to $C_4^-$ for the various modified zeolites were found to decrease in the following order:

$$Ba > La > Ag > Cu > Ca > Sr > Ga > Cd > In$$

Ba, La and Ag exhibited better overall yields of olefins than unmodified S-115 while addition of the other modifiers led to a decrease in the amounts of olefins formed in the reaction products. The light olefin fraction produced in the case of Ba-, La-, Ag- and Cu-modified catalysts consisted mainly of

Table 4.4 : Effect of Promoters on the Performance of Silicalite S-115 at 375 °C, 4 $hr^{-1}$ WHSV and 2.67 methanol to nitrogen (wt/wt) ratio

| PARAMETERS | Promoter (5% Impregnation) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | - | Ba | La | Ag | Cu | Ca | Sr | Ga | Cd | In |
| **Total Life-on-stream (h)** | 67 | 25.5 | 60.5 | 62.5 | 48.25 | 1.75 | 2.5 | 26.0 | 2.58 | 1.35 |
| **Life up to DME(h)** | < 67 | 22.5 | 52.75 | 53.0 | 46.0 | 0.75 | 0.5 | 25.0 | 0.5 | 0.6 |
| **Coke Dep. Rate (wt %/h)** | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 1.4 | 0.7 | 0.2 | 1.9 | 1.9 |
| **Average Conversion (%)** | 92.3 | 90.7 | 91.5 | 92.3 | 92.1 | 85.9 | 79.0 | 91.5 | - | 78.9 |
| ***Light Hydrocarbon Distribution* (*C-wt%*)** | | | | | | | | | | |
| $C_2^-$ | 5.8 | 8.5 | 9.0 | 8.1 | 7.6 | 4.3 | 3.2 | 2.5 | 2.9 | 0.8 |
| $C_3^-$ | 14.4 | 14.9 | 14.4 | 14.6 | 9.6 | 7.2 | 3.7 | 3.2 | 2.1 | 1.1 |
| $C_4^-$ | 12.0 | 14.7 | 14.2 | 13.9 | 11.4 | 6.0 | 3.1 | 3.2 | 1.4 | 0.6 |
| **Total $C_2^-$ – $C_4^-$ Olefins** | **32.2** | **38.1** | **37.6** | **36.6** | **28.6** | **17.5** | **10.0** | **8.9** | **6.4** | **2.5** |
| $C_1$ | 2.6 | 1.9 | 1.3 | 1.4 | 1.2 | 0.4 | 0.2 | 0.2 | 10.0 | 1.0 |
| $C_2$ | 0.6 | 0.7 | 0.4 | 0.3 | 0.2 | 0.0 | 0.0 | 0.1 | 0.1 | 0.8 |
| $C_3$ | 5.9 | 2.1 | 4.3 | 4.3 | 1.9 | 0.2 | 0.6 | 1.2 | 0.1 | 0.1 |
| $C_4$ | 9.6 | 4.6 | 8.2 | 8.1 | 4.1 | 1.4 | 2.4 | 2.1 | 0.0 | 0.2 |
| $C_5$ | 6.6 | 4.8 | 7.4 | 7.3 | 4.8 | 1.6 | 2.0 | 2.0 | 0.6 | 0.4 |
| **Total $C_1$ – $C_5$ Alkanes** | **25.2** | **14.1** | **21.6** | **21.4** | **12.2** | **3.6** | **5.2** | **5.6** | **10.8** | **2.5** |
| $C_2 - C_4$ Olefin Selectivity* | 38.9 | 56.0 | 45.0 | 45.2 | 44.4 | 68.1 | 65.8 | 23.5 | 37.2 | 50.0 |
| ***Product Distribution* (*C-wt%*)** | | | | | | | | | | |
| **Gaseous Hydrocarbons** | 57.4 | 52.2 | 59.2 | 58.0 | 40.8 | 21.1 | 15.2 | 14.5 | 17.2 | 5.0 |
| **Organic Liquids** | 25.4 | 15.8 | 24.4 | 22.9 | 23.6 | 4.6 | 0.0 | 23.4 | 0.0 | 0.0 |
| **Other**** | 17.1 | 32.0 | 16.4 | 19.1 | 35.6 | 74.3 | 84.4 | 62.1 | 82.8 | 95.0 |
| **Water (g/100g MeOH)***** | **47.8** | **41.7** | **37.2** | **42.3** | **43.6** | **35.6** | **18.5** | **43.7** | **0.0** | **28.9** |

* Selectivity = (Olefins/Total Hydrocarbons) x 100

** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether

*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted(g)) x 100

propylene and butenes. On the other hand, Sr-, In- and Cd had the light olefins evenly distributed. Yields of alkanes for the modified zeolites were generally lower than the fresh S-115 and ranged between 2.5 and 21.6% with In and La giving highest and lowest alkane yields respectively. The light alkanes produced consisted mainly of the heavier $C_3$ - $C_5$ alkanes. The ratio of olefins/alkanes was however improved by all modifiers except In and Cd, which exhibited least activity and selectivity to lower olefins in the conversion reaction.

The product distributions for the various catalysts (calculated as g of component produced per 100 g of methanol fed), are illustrated in Figure 4.6 and arranged in decreasing order of total light olefin yields. Water constituted a large part of the products which was evident from the known reaction sequence of the methanol conversion. The first step in the conversion reaction is methanol dehydration to dimethylether which then undergoes additional water-elimination reaction to form hydrocarbons. This accounts for the high proportion of water in the products of the various catalysts.

With respect to the amounts of liquid hydrocarbons formed however, the case of Sr-, In- and Cd-modified catalysts seems unique. In the former two, no liquid hydrocarbons were formed in the product mixture whereas with respect to Cd the products were all in the gaseous phase and no liquids were detected. Two properties common to these elements, is that they all belong to the fifth period in the periodic table of elements and in addition they posses $5s^2$ orbitals in their electronic configurations. Although Ag also belongs to the fifth period, it is characterized by a $5s^1$ orbital and therefore exhibits a much different product spectrum as its counterparts in the period. The absence of organic

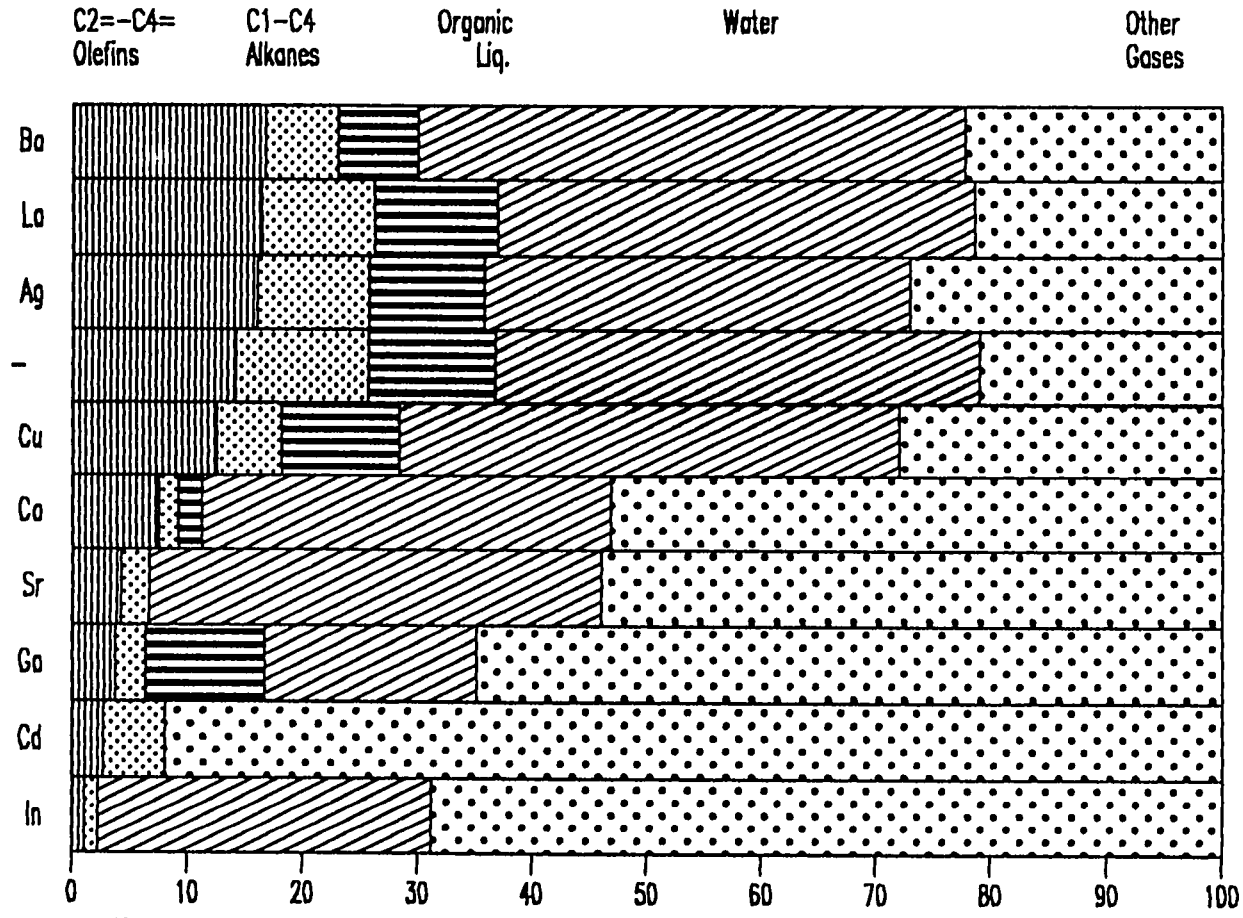



Figure 4.6 : Effect of Impregnation With Various Promoters on Product Distribution for Silicalite S-115 at 400°C and 4 $hr^{-1}$ WHSV

liquids in the Cd-, In- and Sr-modified zeolites might be related in a way to the electronic configuration of the individual elements. La, Ag, Cu and Ga gave approximately the same yields of organic liquids ranging between 22.9 - 24.4% while Ba and Ca had yields of organic liquids of 15.8 and 4.6% respectively.

The amount of other gases formed also varied according to the type of promoter used. These gases consisted of undetectable components such as CO, $CO_2$, $H_2$, and $O_2$ as well as gaseous hydrocarbons that were detectable by the GC-FID detector but not quantifiable as they lied outside the range of the GC calibration mixture.

### *Carbon Deposition and Life on Stream*

Rates of carbon deposition was between 0.1 and 1.9 wt%/h with In- and Cd-modified S-115 showing highest rates. A plot of the rate of coking versus total active lifetime on stream is shown in Figure 4.7. Irrespective of the promoter type, the active life time of the various modified catalysts decreased steadily as the rate of coke formation increased. Ag- , La- and Cu-modified catalysts which had the least coking rates lasted longest before deactivation. The life time of the modified catalysts seemed to have decreased exponentially as a function of the rate of coke deposition following an expression of the form $y = ke^{-ax}$. A non-rigorous least square fitting showed that values of $k = 25.24$ and $a = 0.5$ gave a good fit within the range of coking rates greater than 0.17 wt%/h. Below 0.17 wt%/h however, the active life-on-stream becomes insensitive to the rate of coking and is probably determined largely by catalyst intrinsic properties.

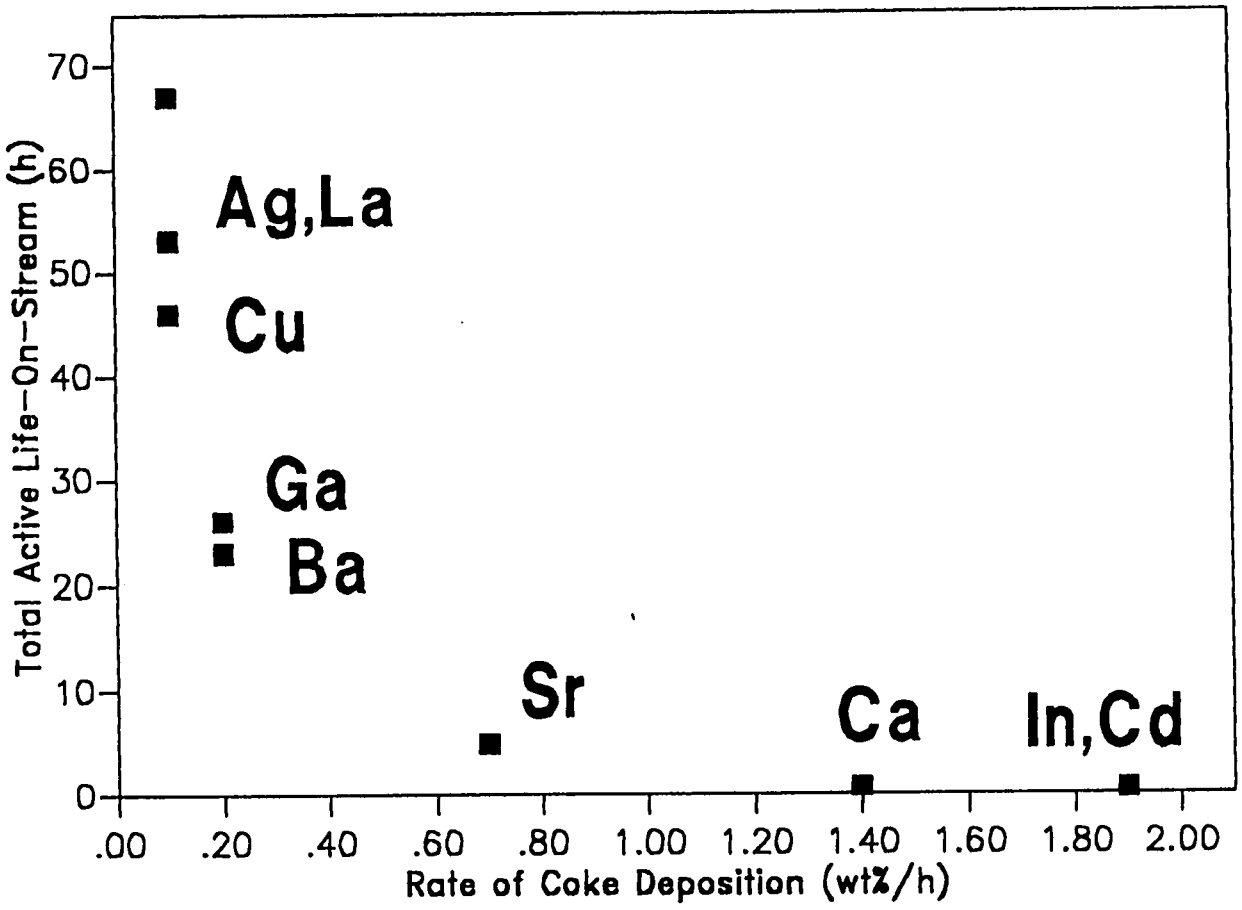



**Figure 4.7 : Total Active Lifetime Versus Rate of Coke Formation (Catalyst wt%/hr) for Various Modifications of S-115**

The relatively faster rates of deactivation of the modified catalysts can be attributed to diffusional constraints caused by incorporation of the modifiers into the inter-crystalline spaces and pore entrances leading to poisoning of active catalytic sites as well as blockade of channel entrances. Coke formation is known to be favoured under such conditions.

The yields of olefins as a function of life-on-stream of the various modified zeolites are presented in Figures 4.8 a and b. Ag and La modified catalysts, showed similar performance as the unmodified S-115 in terms of olefin yield as a function of reaction time (Figure 4.8 a). The two catalysts exhibited similar product distributions, and comparable active life time and rates of coke formation. For both catalysts, the yield of olefins increased steadily until a maximum was reached after about 53 hours of reaction time before deactivation started. Sr and Cd (Figure 4.8a) showed peaks at initial reaction time within the first 1/2 hour but lost activity rapidly as the reaction continued. Ca- and In-modified catalysts showed similar performance as Sr and Cd with total active life of 0.6 and 0.75 hrs respectively before dimethylether appearance (Figure 4.8b). Ga-modified catalyst had a relatively constant yield of olefins for most of the reaction time and maintained slow deactivation trend even after dimethylether appearance. A comparable performance was noted in the Cu-modified catalyst although the overall olefin yield and lifetime were higher than in the case of Ga.

Ba modification (Figure 4.8b) lead to a rapid increase in olefin yield in the initial stage of reaction time reaching a peak of 47% at 17 hours of time-on-stream before deactivation. The first DME peak was however observed after

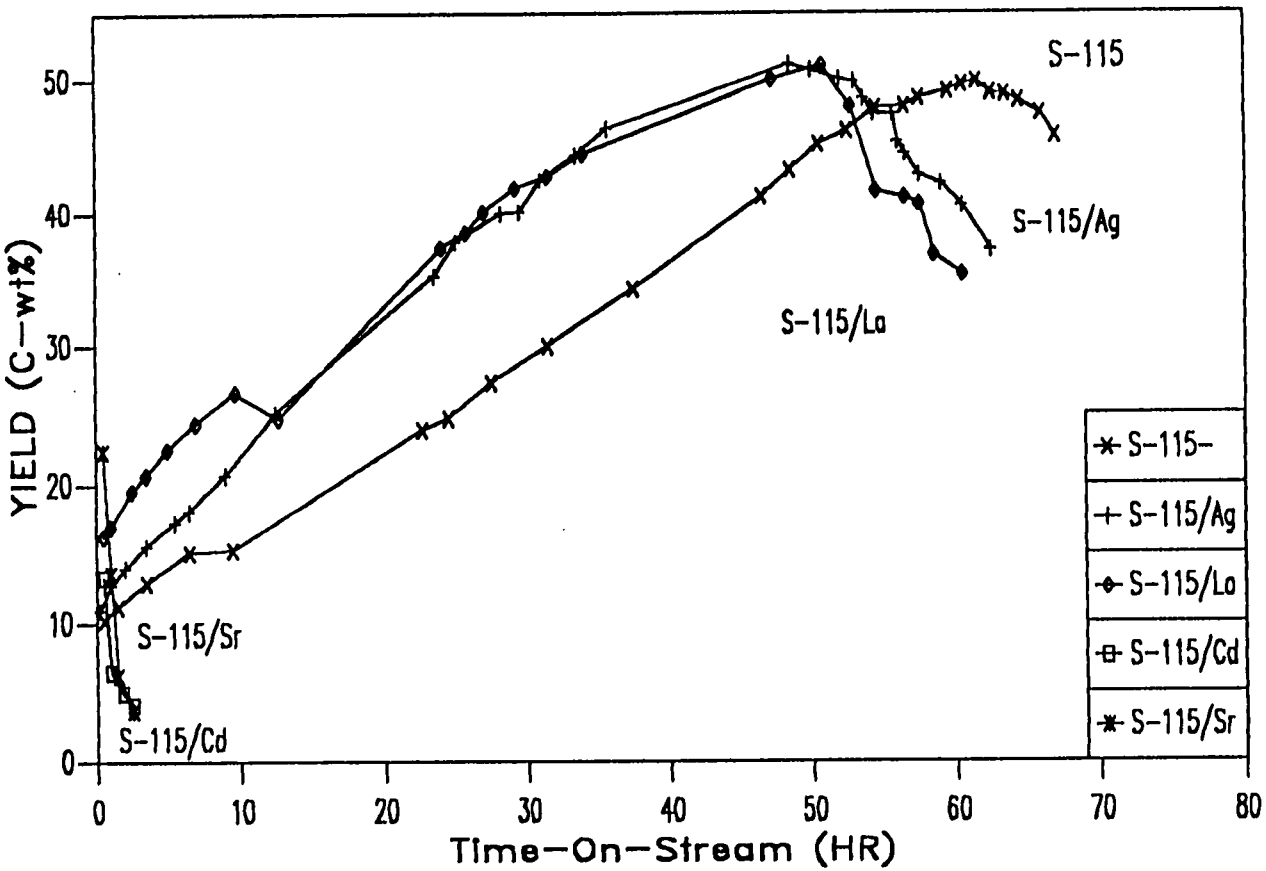



Figure 4.8a: Total Olefin Yields For Various Modifications of S-115 at 400°C 4hr$^{-1}$WHSV and 2.67 MeOH/N (wt/wt) ratio

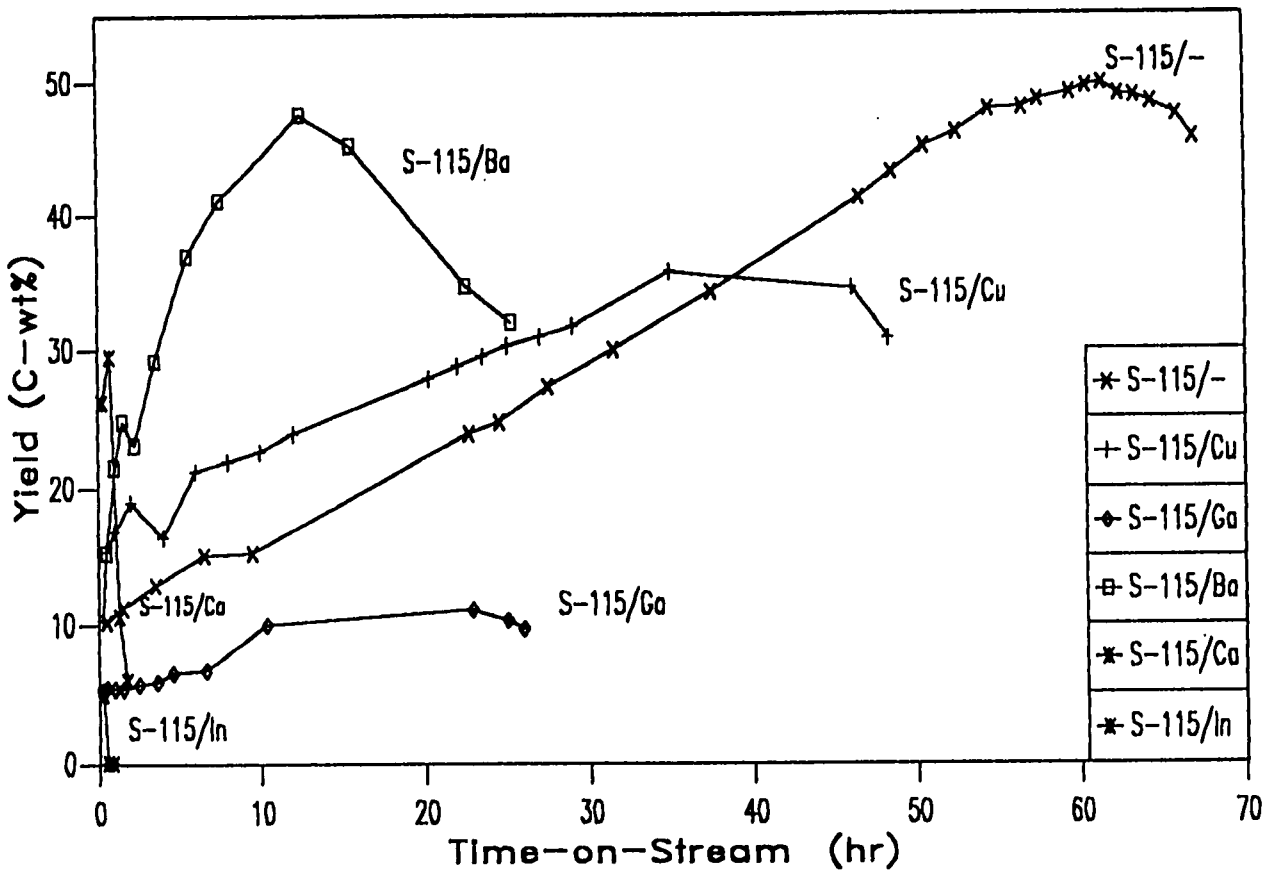



Figure 4.8b : Total Olefin Yields For Various Modifications of S-115 at 400°C ,4 $hr^{-1}$ WHSV and 2.67 MeOH/N (wt/wt) ratio

22.5 hours indicating that for S-115 catalyst, dimethylether may be delayed in some cases until the catalyst deactivates below some tolerable limit.

## *4.3 Parametric Studies on Process Variables*

Parametric studies were carried out to investigate the effect of temperature, space velocity and methanol/nitrogen feed ratio on the performance of ZSM-5 and S-115 on the MTO conversion reaction. The objective was to identify process conditions and reaction parameters that prove most favourable for the conversion reaction. Experiments were carried out according to the scheme shown in Table 4.5. Single parameter variation technique was employed.

### 4.3.1 Effect of temperature .

The effect of temperature on the performance of ZSM-5 and S-115 was studied at atmospheric pressure between 350 and 550°C with the space velocity and methanol/nitrogen (wt) ratio fixed at $4hr^{-1}$ and 2.7 respectively. The space velocity and methanol/nitrogen ratio were chosen based on results previously published {62,103}. Results for the two catalysts are presented in Tables 4.6 - 4.7 and illustrated in Figures 4.9 - 4.12.

Temperature, being a prominent reaction parameter, has pronounced effect on the product distribution in the conversion of methanol to hydrocarbons. Selectivity has been found to be favoured under high temperatures largely due to secondary cracking reactions {9,10}. However, increasing the temperature also leads simultaneously to decomposition of methanol producing methane, $H_2$, and CO {103}. This was evident in both ZSM-5 and S-115 where the methane selectivity jumped from about 3% to 29.1 and 42.3% respectively as the temperature was changed from

**TABLE 4.5 :** Experimental Scheme For Parametric Studies

| Run # | T (°C) | WHSV ($h^{-1}$) | MeOH/ /$N_2$ |
|---|---|---|---|
| 1 | T1 | WHSV1 | R1 |
| 2 | T2 | WHSV1 | R1 |
| 3 | T3 | WHSV1 | R1 |
| 4 | T4 | WHSV1 | R1 |
| 5 | T5 | WHSV1 | R1 |
| | $T_{opt}$ | | |
| 6 | $T_{opt}$ | WHSV2 | R1 |
| 7 | $T_{opt}$ | WHSV3 | R1 |
| 8 | $T_{opt}$ | WHSV4 | R1 |
| | | $WHSV_{opt}$ | |
| 9 | $T_{opt}$ | $WHSV_{opt}$ | R2 |
| 10 | $T_{opt}$ | $WHSV_{opt}$ | R3 |
| 11 | $T_{opt}$ | $WHSV_{opt}$ | $R_{opt}$ |

T = Temperature
WHSV = Weight Hourly Space Velocity
R = Ratio
opt = optimum

450 and 475 °C to 550 °C (Tables 4.6 and 4.7). Furthermore, the decrease in both propylene and butylene and simultaneous increase in ethylene within the temperature range investigated, reflects autocatalysis {62} as well as a lower reactivity of ethylene than the reactivities of propylene and butylene {106}.

*a. ZSM-5*

Yields of total olefins varied between 2.6 and 11.9% within the range of temperature investigated with a gradual increasing trend with temperature. (Table 4.6 and Figures 4.9 - 4.10). In general however, ethylene and propylene yields increased whereas butylene decreased. The yields of alkane fractions consisted mainly of $C_3$ - $C_5$ alkanes and ranged between 43.5 and 49.4% except at 500°C where the yield was recorded as 13.9%. The ratio of olefins to alkanes decreased from 0.2 to 0.1% within the range 350 – 400°C and then steadily increased to 0.3 as the temperature was raised to 550°C. This was expected in view of the corresponding decrease in saturated hydrocarbons which are known to undergo cracking reactions at high temperatures leading to formation of lower olefins and paraffins.

Rate of coke deposition ( wt%/h ) increased monotonically from 0.3 to 1.8 as the temperature increased from 350 to 550°C. On the other hand, the catalyst life time decreased from 34 to 10.3 h within the same temperature range. These results confirmed that the selectivity of ZSM-5 to light olefins can be enhanced at high temperatures. However, a compromise between selectivity and coke deposition has to be established. Based on these results, it was concluded that 450°C was the optimum temperature at which active lifetime and light olefin

Table 4.6 : Effect of Temperature on the Performance of ZSM-5 at 4 $hr^{-1}$ WHSV and 2.67 methanol-to-nitrogen (wt/) ratio

| PARAMETERS | Temperature °C | | | | |
|---|---|---|---|---|---|
| | 350 | 400 | 450 | 500 | 550 |
| **Total Life-on-stream (h)** | 34 | 22.5 | 25.5 | 14.25 | 10.33 |
| **Life up to DME(h)** | 22.75 | 17.0 | 24.0 | 14.25 | 10.33 |
| **Coke Dep. Rate (wt%/h)** | 0.3 | 0.5 | 0.6 | 1.2 | 1.8 |
| **Average Conversion (%)** | 88.1 | 89.1 | 90.1 | 90.4 | 90.72 |
| ***Light Hydrocarbon Distribution* (*C-wt%*)** | | | | | |
| $C_2^-$ | 2.0 | 0.7 | 2.7 | 1.3 | 5.3 |
| $C_3^-$ | 2.6 | 0.7 | 4.5 | 1.4 | 5.2 |
| $C_4^-$ | 2.3 | 1.2 | 2.7 | 1.1 | 1.4 |
| **Total $C_2^-$ – $C_4^-$ Olefins** | **6.9** | **2.6** | **9.9** | **3.8** | **11.9** |
| $C_1$ | 1.9 | 3.8 | 6.2 | 3.1 | 29.1 |
| $C_2$ | 0.6 | 1.1 | 1.3 | 0.6 | 2.6 |
| $C_3$ | 12.6 | 17.1 | 15.4 | 4.3 | 7.5 |
| $C_4$ | 19.2 | 17.4 | 17.8 | 4.2 | 3.2 |
| $C_5$ | 11.3 | 6.8 | 8.7 | 1.7 | 1.1 |
| **Total $C_1$ – $C_5$ Alkanes** | **45.6** | **46.2** | **49.4** | **13.9** | **43.5** |
| **$C_2$–$C_4$ Olefin Selectivity(%)*** | **7.9** | **3.6** | **10.6** | **9.4** | **13.3** |
| ***Product Distribution* (*C-wt%*)** | | | | | |
| **Gaseous Hydrocarbons** | 52.5 | 48.8 | 59.3 | 17.7 | 55.4 |
| **Organic Liquids** | 34.5 | 23.9 | 33.7 | 22.6 | 34.4 |
| **Other**** | 13.0 | 27.3 | 7.0 | 59.7 | 10.2 |
| **Water (g/100g MeOH)***** | **34.1** | **38.7** | **40.6** | **39.8** | **30.7** |

* Selectivity = (Olefins/Total Hydrocarbons)x100
** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether
*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

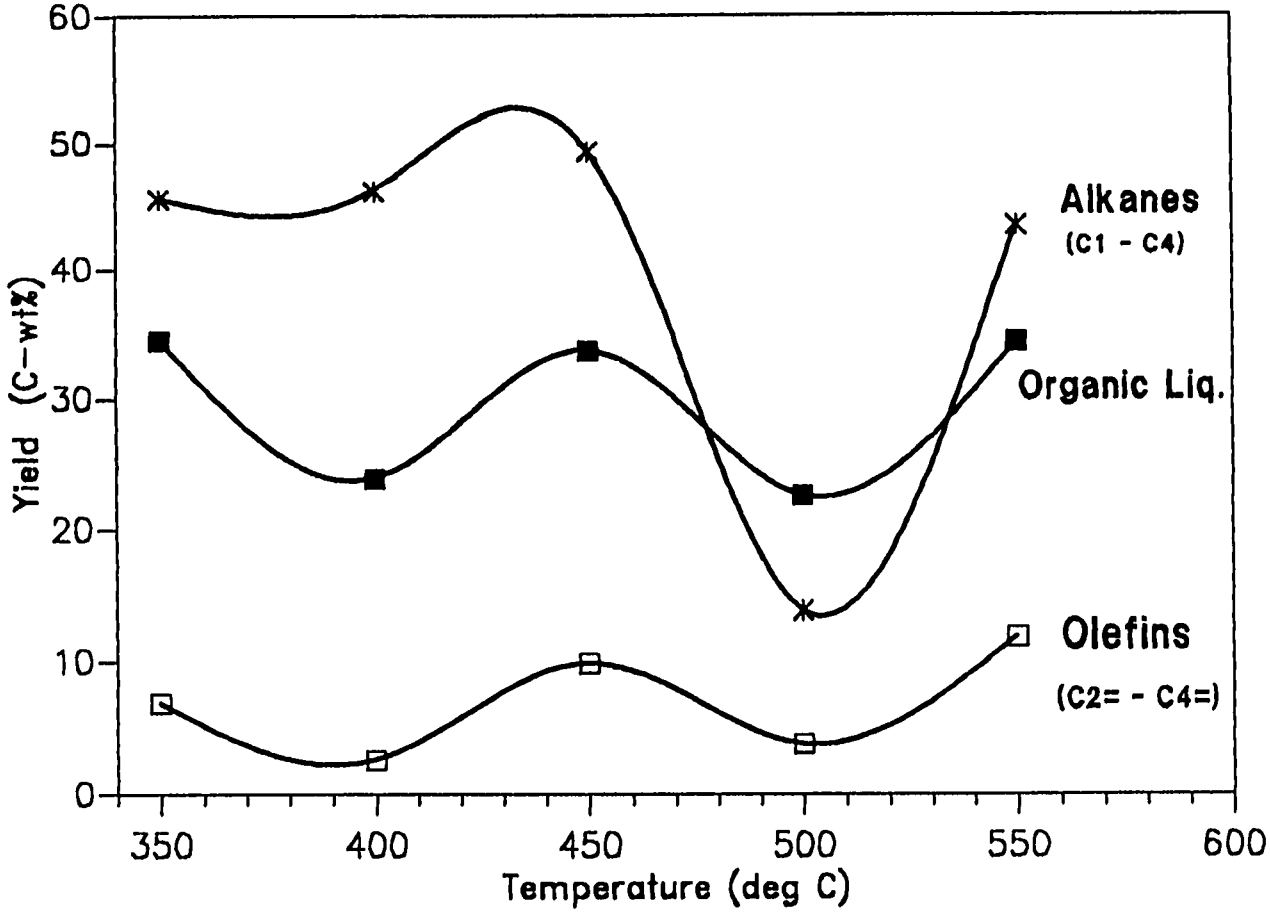



Figure 4.9 : Product Distribution Versus Temperature For ZSM-5 at $4h^{-1}$ WHSV and 2.7 Methanol-to-Nitrogen (wt) Ratio.

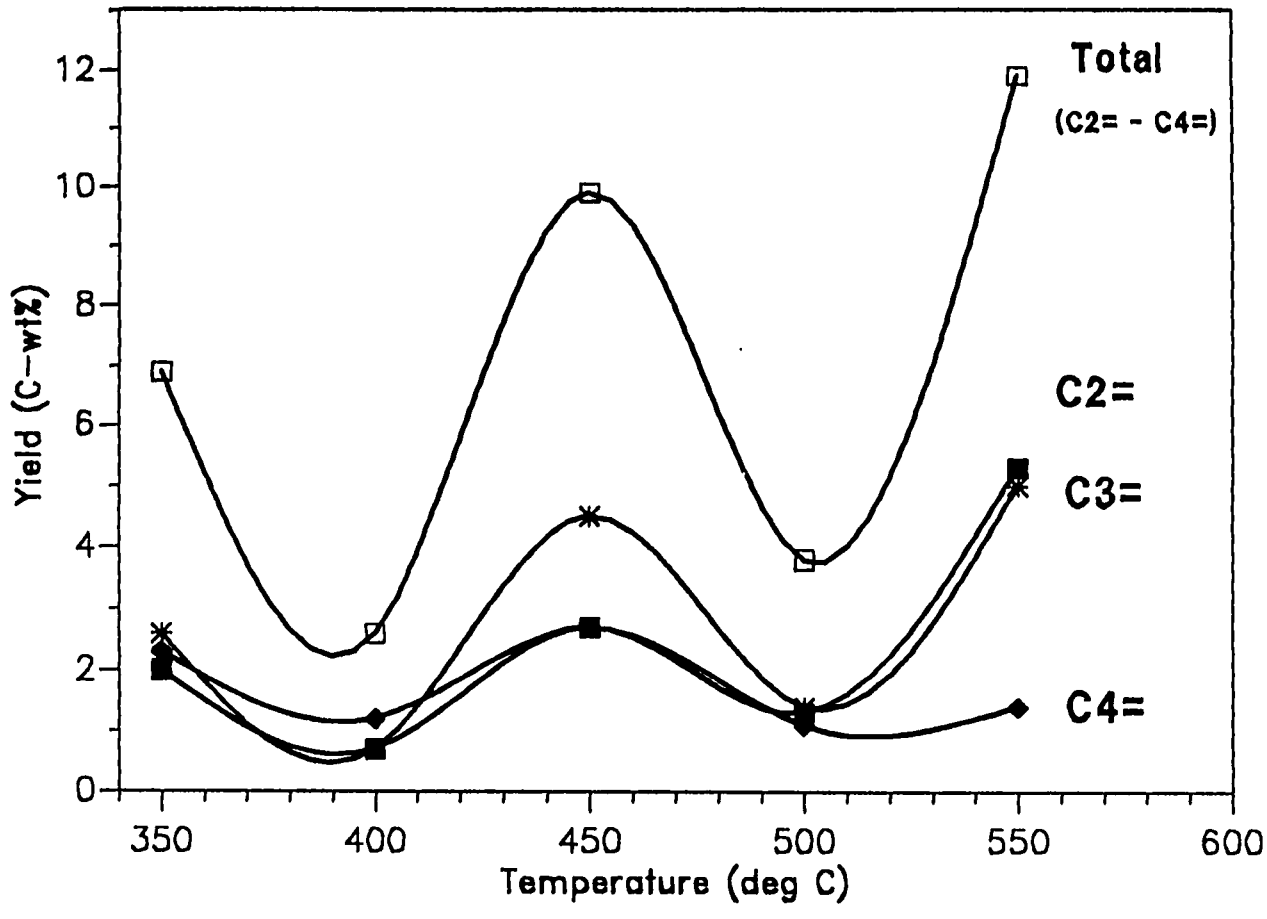



Figure 4.10: Effect of Temperature on Light Olefins Distribution For ZSM-5 at 4h$^{-1}$ WHSV and 2.7 Methanol-to-Nitrogen (wt) Ratio

yield were maximized at moderate coke deposition rate.

### *b. Silicalite S-115*

The effect of temperature on the performance of S-115 was studied between 350 and 550 °C. The catalyst performance was evaluated in terms of product distribution, selectivity to light olefins, coke deposition and active life-on-stream.

The experimental data are shown in Table 4.7 and Figures 4.11 - 4.12. Total yield of light olefins increased from 30.9% at 350°C to a maximum of 35.8 at 375°C and then decreased in a continuous trend, to 3.0% at 550°C. The selectivity to $C_2$ to $C_4$ olefins followed the same trend as the total light olefin yield and ranged between 5.6 and 40.6% with maximum value also occuring at 375°C. Ethylene yield remained relatively constant between 350 and 475°C, dropping to 1.1% as the temperature was increased to 550°C. Yields of propylene and butylenes however followed a similar trend as the total olefins with maximum yields of 15.0% and 14.4% respectively occuring at 375°C (Figure 4.12).

The total alkane yield increased steadily from 18.9 to 45.5% as the temperature varied between 350 and 550°C. A steady shift to lower alkanes was observed as the temperature was raised with a significant methane disproportionation at 550°C. This can be attributed to cracking reactions of the heavier $C_3$ - $C_5$ alkanes and other hydrocarbons. This might also account for the higher rates of coke deposition at 550°C. which exhibited a sudden increase

Table 4.7 : Effect of Temperature on the Performance of Silicalite S-115 at 4 hr $^{-1}$ WHSV and 2.67 methanol-to-nitrogen (wt) ratio

| PARAMETERS | Temperature °C | | | | |
|---|---|---|---|---|---|
| | 350 | 375 | 400 | 475 | 550 |
| **Total Life-on-stream (h)** | 66 | 58.1 | 67 | 51.75 | 27.33 |
| **Life up to DME(h)** | 60 | < 58 | < 67 | 50 | < 27.33 |
| **Coke Dep. Rate (wt%/h)** | 0.1 | 0.2 | 0.1 | 0.2 | 0.5 |
| **Average Conversion (%)** | 92.3 | 90.7 | 92.3 | 90.8 | 99.0 |
| ***Light Hydrocarbon Distribution (C-wt%)*** | | | | | |
| $C_2^=$ | 5.9 | 6.4 | 5.8 | 5.1 | 1.1 |
| $C_3^=$ | 12.4 | 15.0 | 14.4 | 9.3 | 1.4 |
| $C_4^=$ | 12.6 | 14.4 | 12.0 | 9.5 | 0.5 |
| **Total $C_2^= - C_4^=$ Olefins** | **30.9** | **35.8** | **32.2** | **23.9** | **3.0** |
| $C_1$ | 1.7 | 2.6 | 2.6 | 3.0 | 42.3 |
| $C_2$ | 0.4 | 0.6 | 0.6 | 0.7 | 1.8 |
| $C_3$ | 4.8 | 5.4 | 5.9 | 6.5 | 0.9 |
| $C_4$ | 4.6 | 9.3 | 9.6 | 8.7 | 0.4 |
| $C_5$ | 7.4 | 7.1 | 6.6 | 5.6 | 0.1 |
| **Total $C_1 - C_5$ Alkanes** | **18.9** | **25.0** | **25.3** | **24.5** | **45.5** |
| **$C_2 - C_4$ Olefin Selectivity(%)*** | 32.9 | 40.6 | 38.8 | 31.2 | 5.6 |
| ***Product Distribution (C-wt% )*** | | | | | |
| **Gaseous Hydrocarbons** | 49.8 | 60.8 | 57.5 | 48.4 | 48.5 |
| **Organic Liquids** | 44.1 | 27.3 | 25.4 | 28.1 | 5.1 |
| **Other **** | 6.1 | 11.9 | 17.1 | 23.5 | 46.4 |
| **Water (g/100g MeOH)***** | 44.1 | 48.8 | 47.7 | 40.9 | 9.0 |

* Selectivity = (Olefins/Total Hydrocarbons)x100

** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether

*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

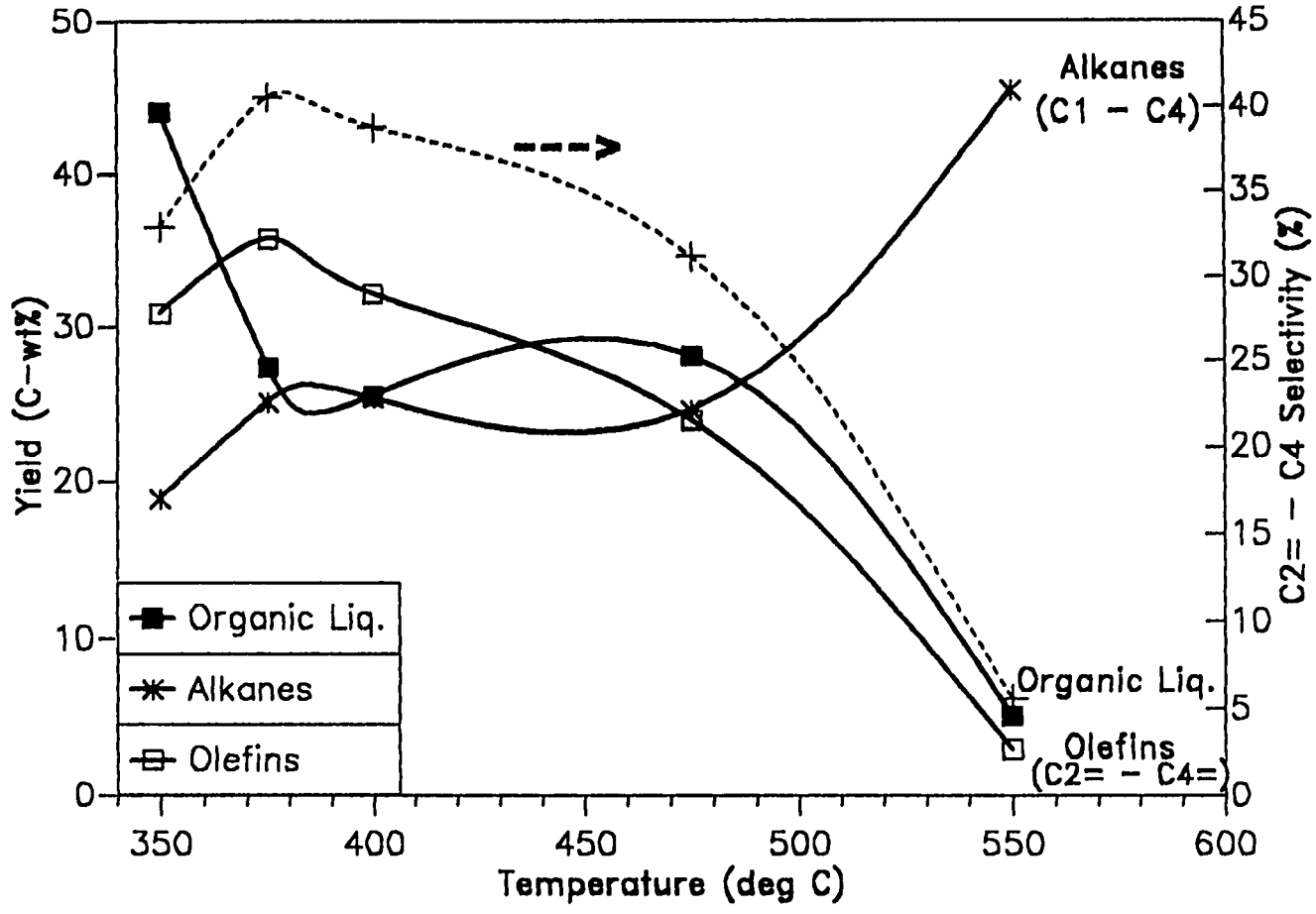



Figure 4.11: Effect of Temperature on Product Distribution for S-115 at 4h$^{-1}$ WHSV and 2.7 Methanol-to-nitrogen (wt) Ratio

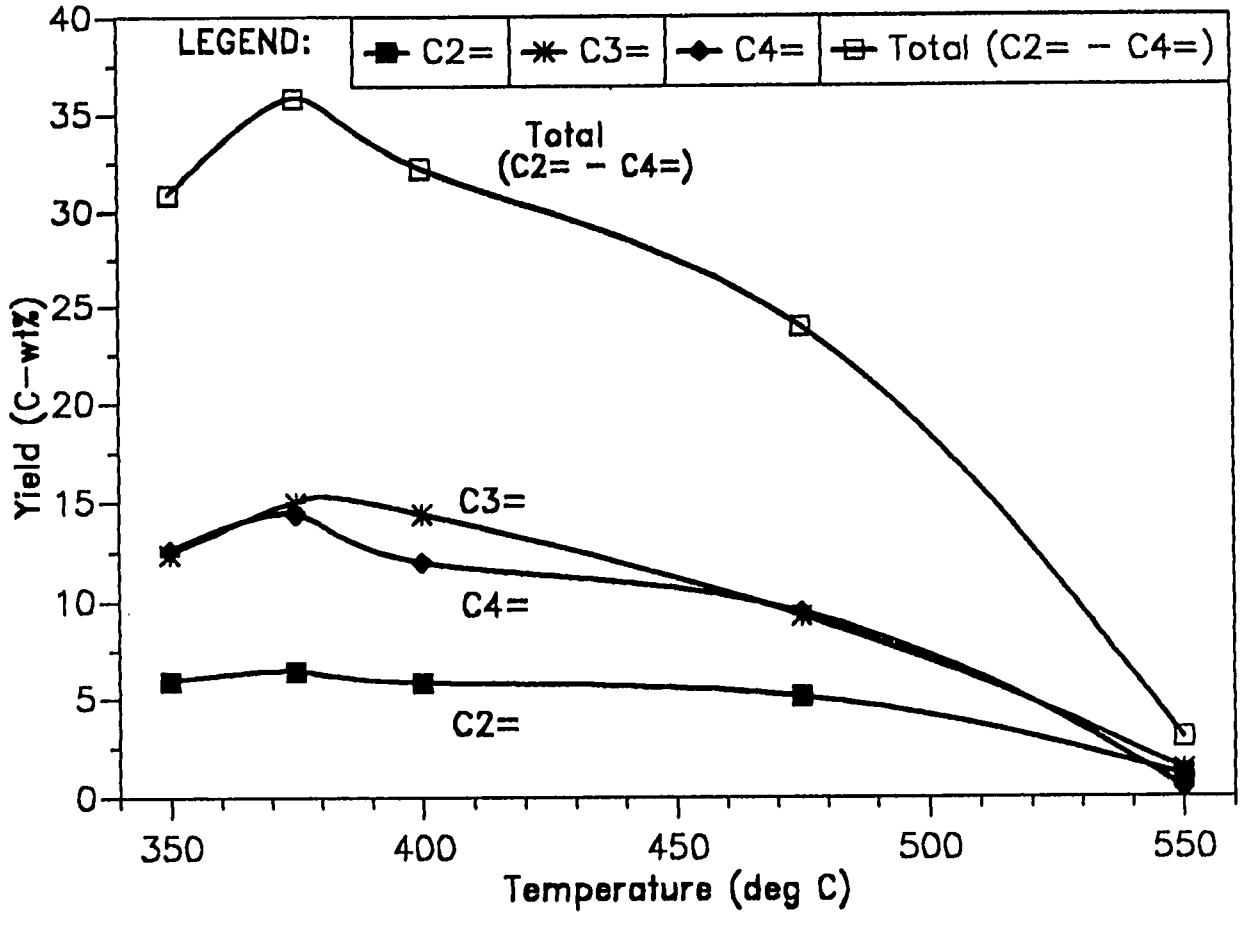



Figure 4.12: Effect of Temperature on Light Olefin Distribution For S-115 at $4h^{-1}$ WHSV and 2.7 Methanol-to-Nitrogen (wt) Ratio

to 0.5 wt%/h from an average of 0.1 - 0.2 wt%/hr between 350 and 475 °C. The catalyst lifetime decreased from 60 - 67 hours at 350 - 400°C. to less than 27.3 hours at 550°C.

The experimental data thus indicated that silicalite S-115 can be best used between 350 and 475 °C. for high olefin yields. However, to optimize both olefin selectivity and catalyst life as well as reduce coke deposition, the optimum* operating temperature should be 375 °C.

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* Optimum relative to the experimental set-up and optimization scheme used. Identification of absolute optimum would require much more experimental work.

### 4.3.2. Effect of Space Velocity

The effect of space velocity on the performance of ZSM-5 and S-115 was studied at optimum temperatures and methanol/nitrogen wt ratio of 2.67. Experiments were carried out at various space velocities to investigate their influence on product distribution, catalyst life and coke deposition.

It is known {13}, that space velocity has a considerable influence on the product spectrum in the MTO conversion due to the sequential nature of the reaction. Since olefins are intermediates in the reaction sequence:

$$\text{Methanol/DME} \rightarrow C_2-C_4 \text{ Olefins} \rightarrow C^+_5 \text{ nonaromatics} \rightarrow \text{aromatics} + \text{paraffins}$$

their selectivity might be enhanced by low contact times {13,103}. This is evident since high space velocity is expected to reduce contact time and hence conversion. This was noted with S-115 catalyst where the least conversion corresponded with the highest space velocity. The effect of space velocity was found to exhibit a synergistic relationship with Bronsted acidity in determining product distribution illustrating a trade-off between the two parameters {41}. In a contrasting study, Hoeldrich et al {62} found $C_2-C_4$ olefin selectivity to be substantially constant over a wide range of space velocities (0.5 - 15 $h^{-1}$). The latter case was explained in terms of the isothermicity of the reaction set-up, whereas in the former, the nature of product distribution obtained by Chang et al {41} was attributed more to the adiabatic conditions of the reaction system. It is thus expected that in a situation where a semi-adiabatic condition

predominates an overlap of the two cases might emerge. This was observed with the data obtained in ZSM-5 and S-115. In the case of ZSM-5, a maximum yield of olefins (9.9%) was obtained at $4h^{-1}$ but the yield dropped to a relatively constant value within the range 5.5 to 8 $h^{-1}$. With S-115 however, a peak was noted between 4 $h^{-1}$ and 5.5 $h^{-1}$ WHSV but the yield continued to decrease upon further increase in space velocity.

Tables 4.8 - 4.9 and Figures 4.13 - 4.16 show the experimental data and product distribution as a function of space velocity.

### *a. ZSM-5*

The effect of space velocity on the performance of ZSM-5 was investigated between 2 - 8 $hr^{-1}$ WHSV at 450°C and atmospheric pressure. The experimental results are tabulated in Table 4.8 and shown graphically on Figures 4.13 -14. The yield of $C_2$ - $C_4$ light olefins ranged between 2.5 and 9.9% with a maximum at $4hr^{-1}$ WHSV. Total $C_1$ - $C_5$ alkanes and organic liquids also had maximum yields of 49.4 and 33.7% respectively at $4hr^{-1}$ WHSV. The active life-on-stream however decreased steadily from 35 hr at $2.5hr^{-1}$ WHSV to 8.7 hr at $8hr^{-1}$ WHSV accompanied by an increase in coke formation as a function of space velocity. The optimum space velocity was therefore chosen to be $4hr^{-1}$ WHSV.

Table 4.8 : Effect of Space Velocity on the Performance of ZSM-5 at 450 °C, and methanol/nitrogen (wt/wt) ratio of 2.67

| PARAMETERS | WHSV (h ) | | | |
|---|---|---|---|---|
| | 2.5 | 4.0 | 5.5 | 8.0 |
| **Total Life-on-stream (h)** | 41.5 | 25.5 | 19.6 | 9.25 |
| **Life up to DME(h)** | 35.0 | 24.00 | 18.75 | 8.67 |
| **Coke Dep. Rate (wt%/h)** | 0.4 | 0.6 | 0.6 | 1.2 |
| **Average Conversion (%)** | 94.2 | 90.14 | 91.7 | 93.39 |
| ***Light Hydrocarbon Distribution (C-wt%)*** | | | | |
| $C_2^=$ | 0.7 | 2.7 | 0.6 | 0.8 |
| $C_3^=$ | 1.1 | 4.5 | 1.0 | 1.2 |
| $C_4^=$ | 0.9 | 2.7 | 0.9 | 1.0 |
| **Total $C_2^= - C_4^=$ Olefins** | **2.7** | **9.9** | **2.5** | **3.0** |
| $C_1$ | 1.1 | 6.2 | 0.8 | 1.4 |
| $C_2$ | 0.4 | 1.3 | 0.3 | 0.4 |
| $C_3$ | 5.1 | 15.4 | 3.2 | 4.3 |
| $C_4$ | 5.1 | 17.8 | 4.6 | 4.5 |
| $C_5$ | 2.6 | 8.7 | 2.7 | 2.8 |
| **Total $C_1 - C_5$ Alkanes** | **14.3** | **49.4** | **11.6** | **13.4** |
| **$C_2 - C_4$ Olefin Selectivity(%)*** | **6.3** | **10.6** | **5.4** | **6.4** |
| ***Product Distribution (C-wt%)*** | | | | |
| **Gaseous Hydrocarbons** | 17.0 | 59.3 | 14.1 | 16.4 |
| **Organic Liquids** | 25.9 | 33.7 | 32.5 | 30.4 |
| **Other **** | 57.1 | 7.0 | 53.4 | 53.2 |
| **Water (g/100g MeOH)***** | **36.5** | **40.1** | **34.7** | **37.2** |

* Selectivity = (Olefins/Total Hydrocarbons)x100
** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether
*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

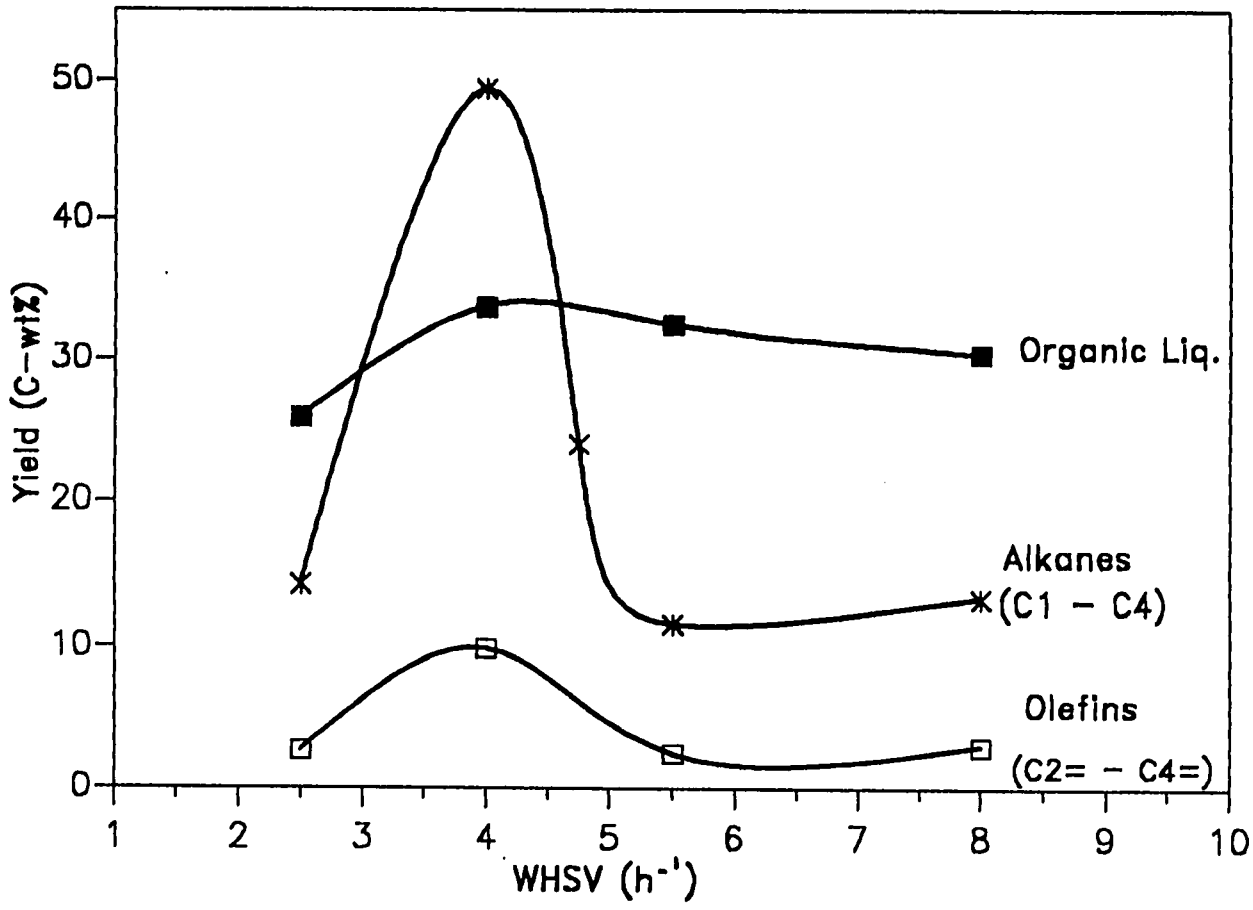


Figure 4.13: Effect of Space Velocity on Product Distribution for ZSM-5 at 450°C and 2.7 Methanol-to-nitrogen (wt) Ratio

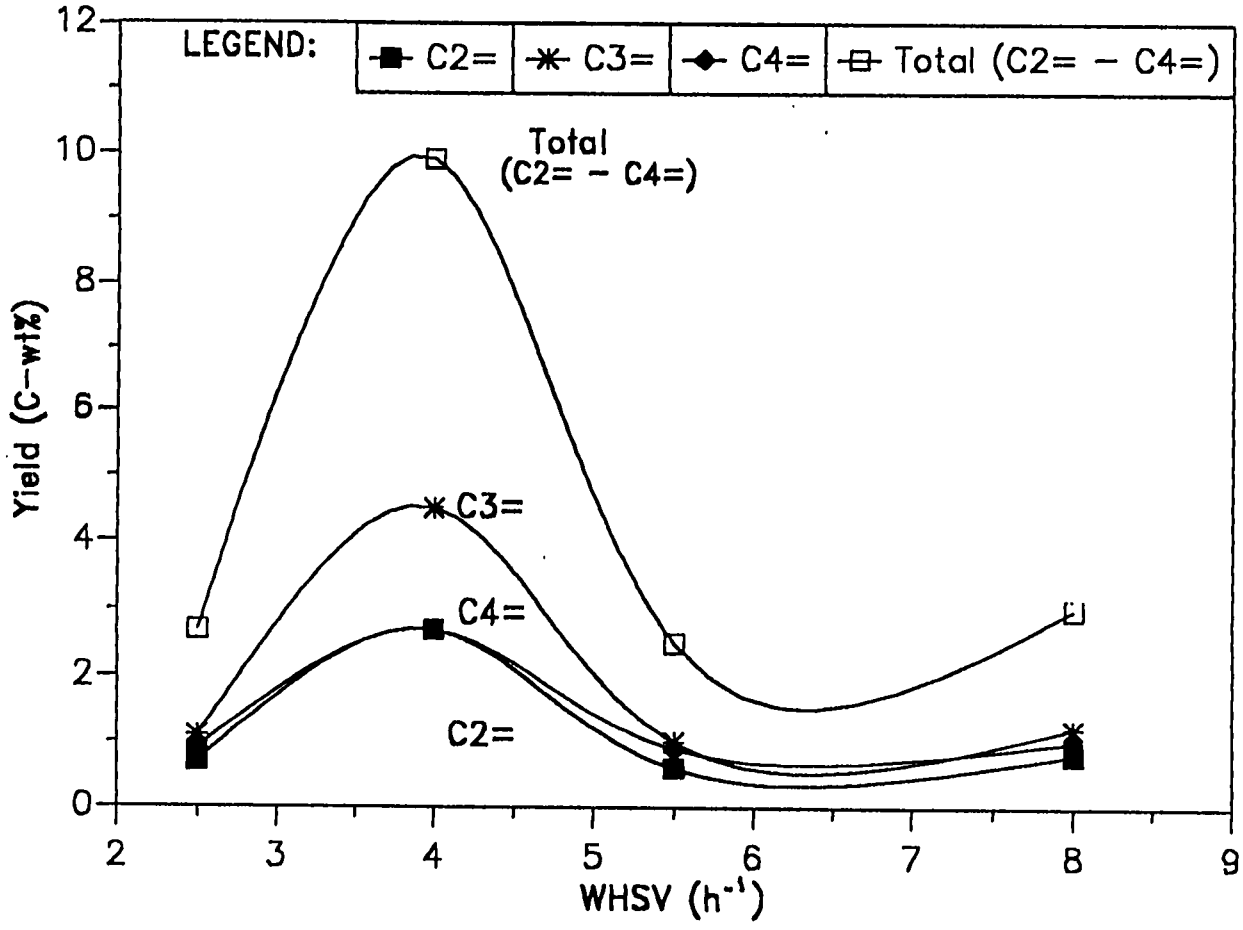


Figure 4.14: Effect of Space Velocity on Yields of Light Olefins for ZSM-5 at 450°C and 2.7 Methanol-to-nitrogen (wt) Ratio

### *b. Silicalite S-115*

The influence of space velocity on the performance of S-115 was studied between 2.5 and 8.0 $hr^{-1}$ WHSV, 375°C, and 2.7 methanol/nitrogen wt ratio. The experimental data are given in Table 4.9 and shown in Figures 4.15 - 4.16.

The experimental results showed that yields of light olefins varied between 18.5 and 37.2% within the range of space velocity investigated. The yield of olefins increased initially reaching a maximum between 4.0 and 5.5 $h^{-1}$ WHSV and then assumed a decreasing trend upon further increase in space velocity. The selectivity to $C_2$ - $C_4$ olefins however increased continuously as a function of space velocity reaching 52.2% at 8.0 $h^{-1}$ WHSV from 22.8% at 4.0 $h^{-1}$ WHSV . This was expected since raising the space velocity normally leads to lowering contact time between the reactants and catalyst bed. The reactions sequence is hence curtailed at the intermediate species resulting in product mixtures containing large proportions of olefins.

Amounts of $C_1$ - $C_5$ alkanes produced on the other hand, decreased steadily from 29.4% at 2.5$hr^{-1}$ WHSV to a minimum of 10% at 8.0$hr^{-1}$ WHSV. The yields of organic liquids followed a similar pattern as the light alkanes with a maximum of 33.7% at 2.5$hr^{-1}$ WHSV and a minimum of 16.4 % at 8.0$hr^{-1}$ WHSV.

Although the yield of olefins at 5.5$hr^{-1}$ WHSV is slightly higher than that at 4.0$hr^{-1}$ WHSV, the difference lies within the range of experimental error. Further, the DME peak for the run at 6.0 $hr^{-1}$ WHSV, appeared much earlier

Table 4.9 : Effect of Space Velocity on the Performance of Silicalite S-115 at 375 °C and 2.67 methanol-to-nitrogen (wt) ratio

| PARAMETERS | WHSV ($h^{-1}$) | | | |
|---|---|---|---|---|
| | 2.5 | 4.0 | 5.5 | 8.0 |
| **Total Life-on-stream (h)** | 137 | 58.1 | 28.75 | 50.00 |
| **Life up to DME(h)** | 135 | < 58 | 11.0 | - |
| **Coke Dep. Rate (wt %/h)** | 0.1 | 0.2 | 0.1 | 0.1 |
| **Average Conversion (%)** | 90.6 | 90.7 | 95.6 | 87.5 |
| ***Light Hydrocarbon Distribution (C-wt%)*** | | | | |
| $C_2^=$ | 3.1 | 6.4 | 8.9 | 8.7 |
| $C_3^=$ | 6.9 | 15.0 | 14.8 | 11.2 |
| $C_4^=$ | 8.5 | 14.4 | 13.5 | 8.9 |
| **Total $C_2^= - C_4^=$ Olefins** | **18.5** | **35.8** | **37.2** | **28.8** |
| $C_1$ | 2.4 | 2.6 | 0.7 | 0.3 |
| $C_2$ | 0.8 | 0.6 | 0.2 | 0.1 |
| $C_3$ | 6.5 | 5.4 | 3.1 | 1.5 |
| $C_4$ | 11.3 | 9.3 | 6.3 | 3.4 |
| $C_5$ | 8.4 | 7.1 | 6.8 | 4.7 |
| **Total $C_1 - C_5$ Alkanes** | **29.4** | **25.0** | **17.1** | **10.0** |
| **$C_2 - C_4$ Olefin Selectivity(%)*** | **22.8** | **40.6** | **46.1** | **52.2** |
| ***Product Distribution (C-wt%)*** | | | | |
| **Gaseous Hydrocarbons** | 47.9 | 60.8 | 54.3 | 38.8 |
| **Organic Liquids** | 33.4 | 27.3 | 26.4 | 16.4 |
| **Other **** | 18.7 | 11.9 | 19.3 | 44.8 |
| **Water (g/100g MeOH)***** | 46.9 | 48.8 | 59.6 | 56.6 |

* Selectivity = (Olefins/Total Hydrocarbons)x100

** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether

*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

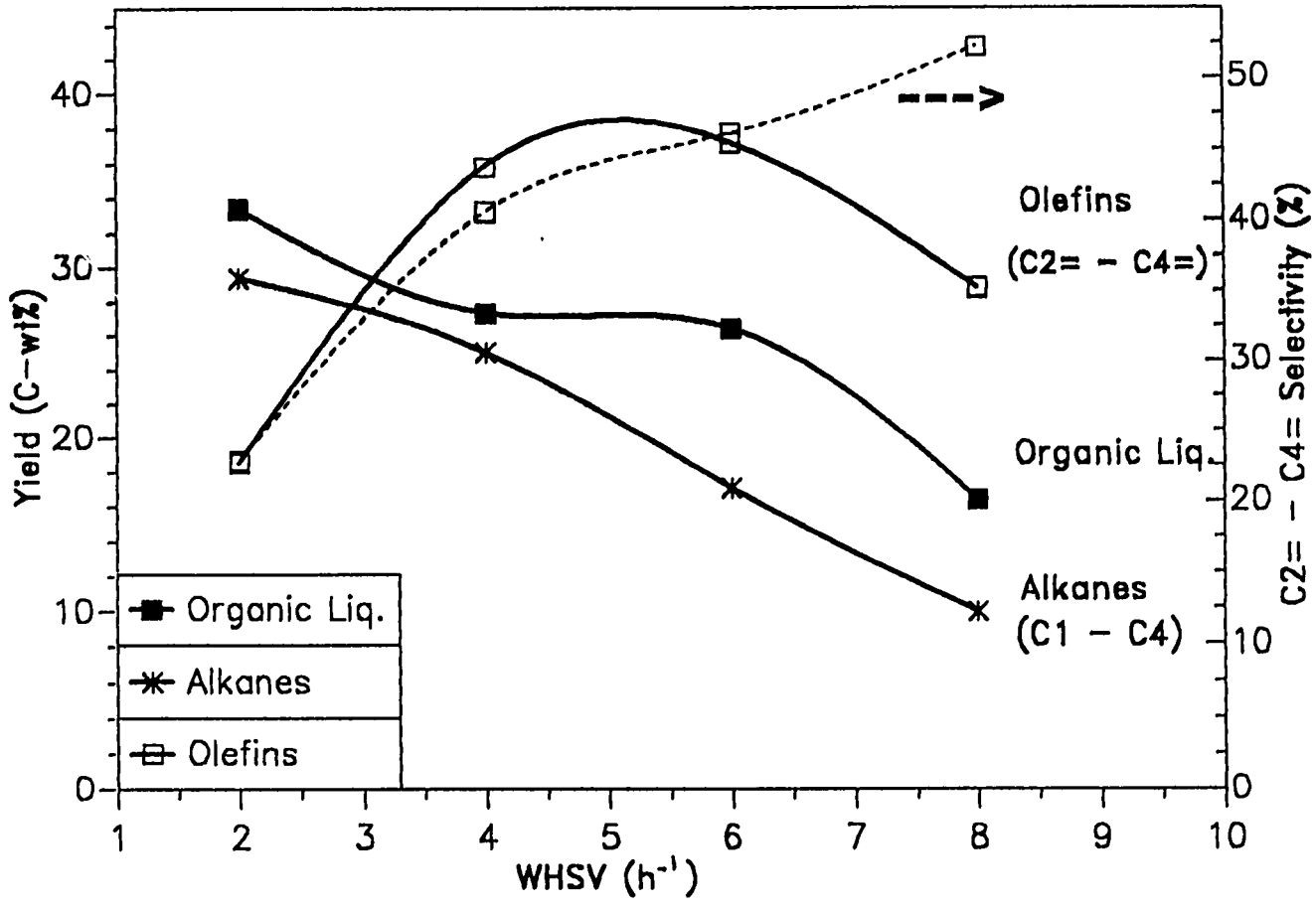


Figure 4.15: Effect of Space Velocity on Product Distribution for S-115 at 375°C and 2.7 Methanol-to-nitrogen (wt) Ratio.

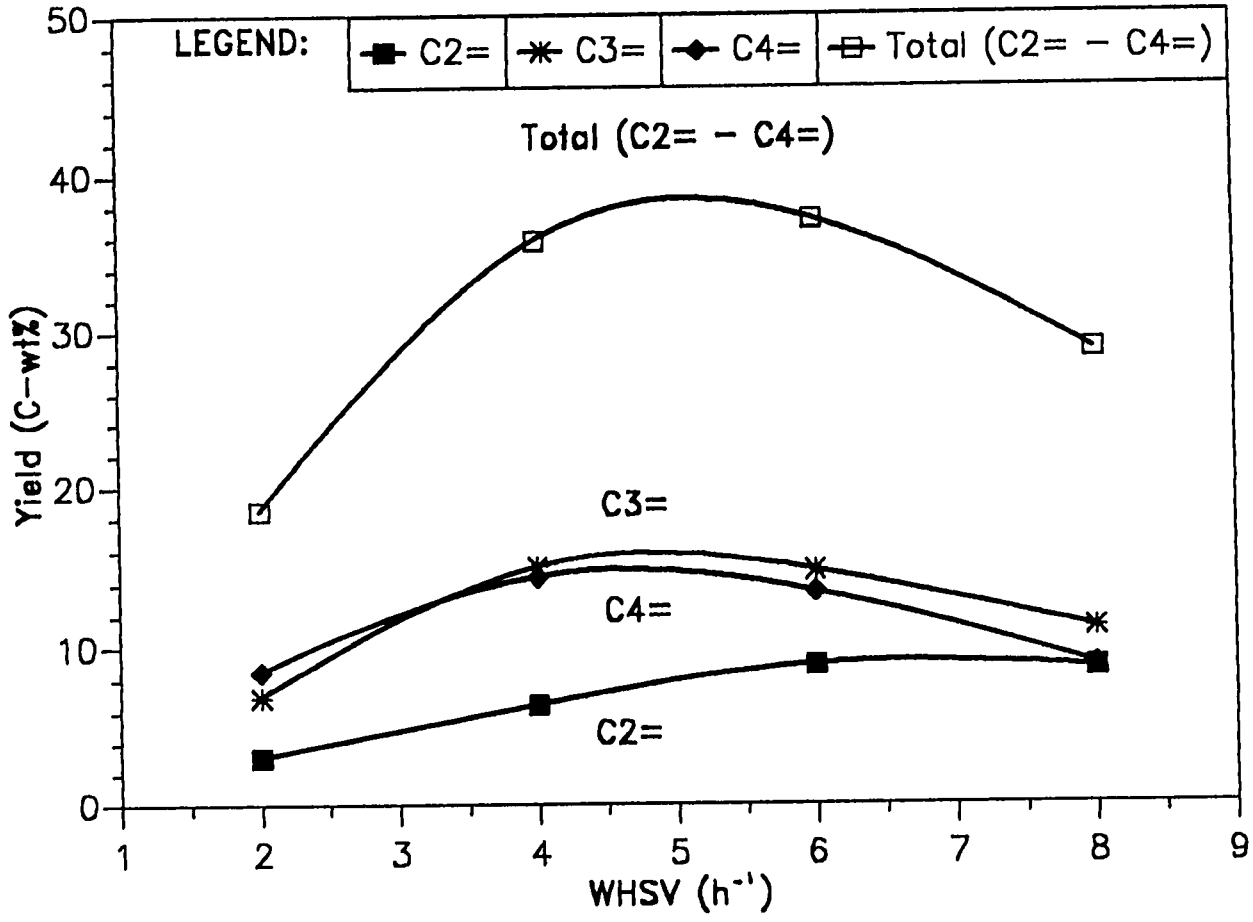


Figure 4.16: Effect of Space Velocity on Yield of Light Olefins for S-115 at 375°C and 2.7 Methanol-to-Nitrogen (wt) Ratio

than the case of 4.0 $hr^{-1}$ WHSV. Therefore based on active life-on-stream, and yield and selectivity to light olefin, the optimum space velocity of fresh S-115 was chosen to be 4.0 $hr^{-1}$ WHSV.

### 4.3.3 Effect of Methanol/Nitrogen Ratio.

High temperature conversion of methanol to olefins over pentasil type zeolites is characterized by significant coke formation particularly with prolonged contact times. Formation of carbonaceous residues result in pore blocking and prevents the access of reactants to the active sites in the intracrystalline volume leading to early deactivation {33}. Nonetheless, active life-on-stream and yields of olefins can be improved by controlling methanol partial pressure as well as residence time through using diluents{107}. In such cases inert gases are usually employed since they are expected not to take part in the conversion reactions.

The effect of methanol/nitrogen ratio on the performance of ZSM-5 and S-115 was studied under optimum conditions of temperature and space velocity. The experimental data for the two catalysts are shown in Tables 4.10 -4.11 and shown graphically on Figures 4.17 - 4.20. In both catalysts, the yields of olefins showed an initial decrease when the methanol/nitrogen (wt) ratio was changed from 0.28 to 0.66 with a simultaneous increase in alkane yields. This could be attributed to decoupling of the reacting step towards paraffins and higher aromatics which is normally enhanced at higher partial pressures {104}.

### *a. ZSM-5*

The effect of methanol/nitrogen ratio on the performance of ZSM-5 was carried out to investigate its effect on product distribution, catalyst life and coke deposition. Experiments were carried out in the range of 0.28 - 2.7 methanol/nitrogen wt ratio. The results are given in Table 4.10 and Figures 4.17 - 4.18.

The experimental results showed that the total light olefin yield decreased to a minimum of 3.1% at 0.66 wt ratio and then increased to 9.9% at 2.7 wt ratio. The individual olefins namely ethylene, propylene and butylene followed the same trend as the total olefin yield. Total $C_1$ - $C_5$ alkanes however ranged between 41.9 % and 50.8 % with a maximum at 0.66 methanol/nitrogen wt ratio. Yield of organic liquids and life-on-stream were highest at 2.7 wt ratio. Coke deposition was however relatively constant within the range of ratios investigated and varied between 0.6 - 0.7 wt%/hr. Hence based on total active life-on-stream and yield of gaseous hydrocarbons, the optimum methanol-to-nitrogen (wt) ratio was selected as 2.7 at 450 °C and 4 $hr^{-1}$ WHSV.

Table 4.10 : Effect of Methanol-to-Nitrogen (wt/) ratio on the Performance of ZSM-5 at 450 °C and 4 $h^{-1}$ WHSV.

| PARAMETERS | Methanol-to-Nitrogen (wt) ratio | | |
|---|---|---|---|
| | 0.28 | 0.66 | 2.67 |
| **Total Life-on-stream (h)** | 23.3 | 22.8 | 25.5 |
| **Life up to DME(h)** | 23.3 | 22.75 | 24.0 |
| **Coke Dep. Rate (wt%/h)** | 0.6 | 0.7 | 0.6 |
| **Average Conversion (%)** | 97.3 | 99.2 | 90.1 |
| ***Light Hydrocarbon Distribution* (*C-wt%*)** | | | |
| $C_2^-$ | 3.9 | 0.8 | 2.7 |
| $C_3^-$ | 6.8 | 1.5 | 4.5 |
| $C_4^-$ | 3.3 | 0.8 | 9.9 |
| **Total $C_2^- - C_4^-$ Olefins** | **14.0** | **3.1** | **9.9** |
| $C_1$ | 4.4 | 6.1 | 6.2 |
| $C_2$ | 1.1 | 1.7 | 1.3 |
| $C_3$ | 12.1 | 19.1 | 15.4 |
| $C_4$ | 18.3 | 19.3 | 17.8 |
| $C_5$ | 6.0 | 4.6 | 8.7 |
| **Total $C_1 - C_5$ Alkanes** | **41.9** | **50.8** | **49.4** |
| **$C_2 - C_4$ Olefin Selectivity(%)*** | **18.7** | **4.2** | **10.6** |
| ***Product Distribution* (*C-wt%*)** | | | |
| **Gaseous Hydrocarbons** | 55.9 | 53.9 | 59.3 |
| **Organic Liquids** | 19.0 | 16.7 | 33.7 |
| **Others**** | 25.1 | 29.4 | 7.0 |
| **Water (g/100g MeOH)***** | 52.2 | 50.4 | 40.1 |

* Selectivity = (Olefins/Total Hydrocarbons)x100
** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether
*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

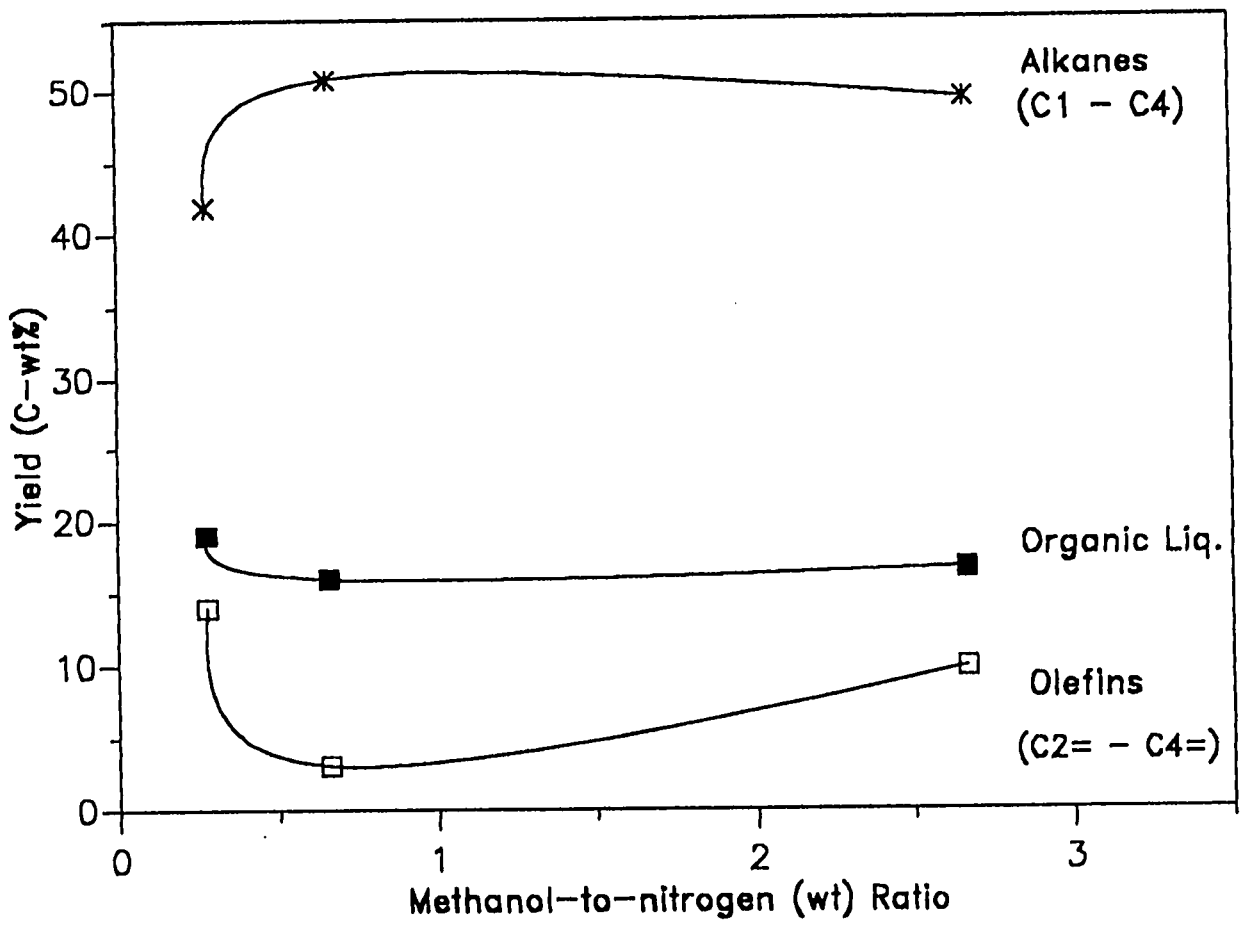


Figure 4.17: Effect of Methanol–to–nitrogen Ratio on Product Distribution for ZSM–5 at 450°C and $4h^{-1}$ WHSV

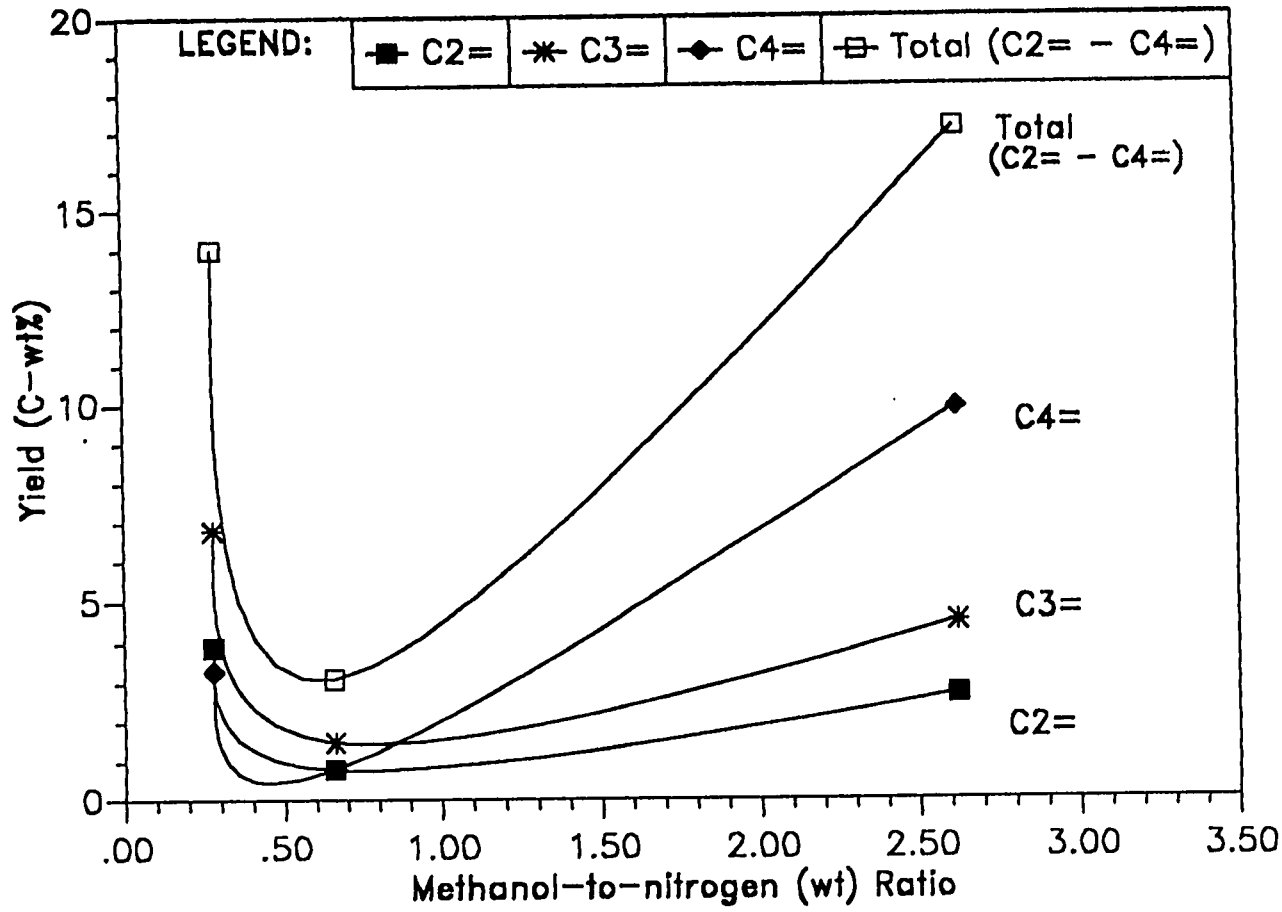


Figure 4.18: Effect of Methanol-to-nitrogen Ratio on Yiled of Light Olefins For ZSM-5 at 450°C and $4h^{-1}$ WHSV.

*b. S-115*

The effect of methanol/nitrogen ratio on the performance of S-115 was investigated at 375°C and $4hr^{-1}$ WHSV. The results are given in Table 4.11 and illustrated graphically on Figures 4.19 - 4.20.

The experimental data showed that yield of total light olefins was inversely related to methanol/nitrogen ratio with a decreasing trend as the methanol/nitrogen ratio increased. Maximum yield of 58.9% occured at 0.28 methanol/nitrogen wt ratio. The yield decreased continuously as the ratio was increased, reaching a minimum value of 25.8% at 2.7 methanol/nitrogen wt ratio. The light olefin selectivity also showed an identical trend as the total $C_2$ - $C_4$ yield with a maximum selectivity of 73.0% occuring at 0.28 methanol-to-nitrogen (wt) ratio, before dropping to 29.3% as the ratio was increased to 2.67. This phenomenon is in agreement with previous works {15,107} suggesting the promoting effect dilution has on light olefin selectivity which was found to result from reduction in reactant partial pressure as well as residence time within the catalyst bed. A major drawback to this method however lies in the necessity to recover products from dilute streams {15}.

The yield of saturated hydrocarbons however showed a direct relation with the methanol/nitrogen ratio and increased from 17.2 to 26.1% as the weight ratio was varied between 0.28 and 2.7. Yield of organic liquids followed a similar pattern as the total $C_1$ - $C_5$ alkanes. Rate of coke deposition was constant at 0.1 wt%/hr between 0.28 and 0.66 wt ratio but increased to 0.2 wt%/hr at 2.7 wt ratio. The total active life-on-stream however did not show a

Table 4.11 : Effect of Methanol-to-Nitrogen (wt) ratio on the Performance of Silicalite S-115 at 375°C and 4 $hr^{-1}$ WHSV

| PARAMETERS | Methanol-to-Nitrogen (wt) ratio | | |
|---|---|---|---|
| | 0.28 | 0.66 | 2.67 |
| Total Life-on-stream (h) | 47.3 | 75.1 | 47.33 |
| Life up to DME(h) | 47.3 | 75.1 | 47.33 |
| Coke Dep. Rate (wt %/h) | 0.1 | 0.1 | 0.2 |
| Average Conversion (%) | 98.5 | 94.8 | 98.5 |
| *Light Hydrocarbon Distribution (C-wt%)* | | | |
| $C_2^=$ | 12.1 | 8.4 | 8.1 |
| $C_3^=$ | 27.9 | 18.4 | 8.2 |
| $C_4^=$ | 18.9 | 18.1 | 9.5 |
| Total $C_2^= - C_4^=$ Olefins | 58.9 | 34.9 | 25.8 |
| $C_1$ | 1.7 | 1.3 | 1.1 |
| $C_2$ | 0.5 | 0.4 | 0.3 |
| $C_3$ | 3.7 | 3.6 | 4.5 |
| $C_4$ | 7.2 | 8.2 | 11.3 |
| $C_5$ | 4.1 | 7.1 | 8.9 |
| Total $C_1 - C_5$ Alkanes | 17.2 | 20.6 | 26.1 |
| $C_2 - C_4$ Olefin Selectivity(%)* | 73.8 | 50.0 | 29.3 |
| *Product Distribution (C-wt%)* | | | |
| Gaseous Hydrocarbons | 76.1 | 55.5 | 51.9 |
| Organic Liquids | 3.7 | 14.3 | 36.2 |
| Others** | 20.2 | 30.2 | 11.9 |
| Water (g/100g MeOH)*** | 53.2 | 48.5 | 52.9 |

* Selectivity = (Olefins/Total Hydrocarbons)x100
** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether
*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

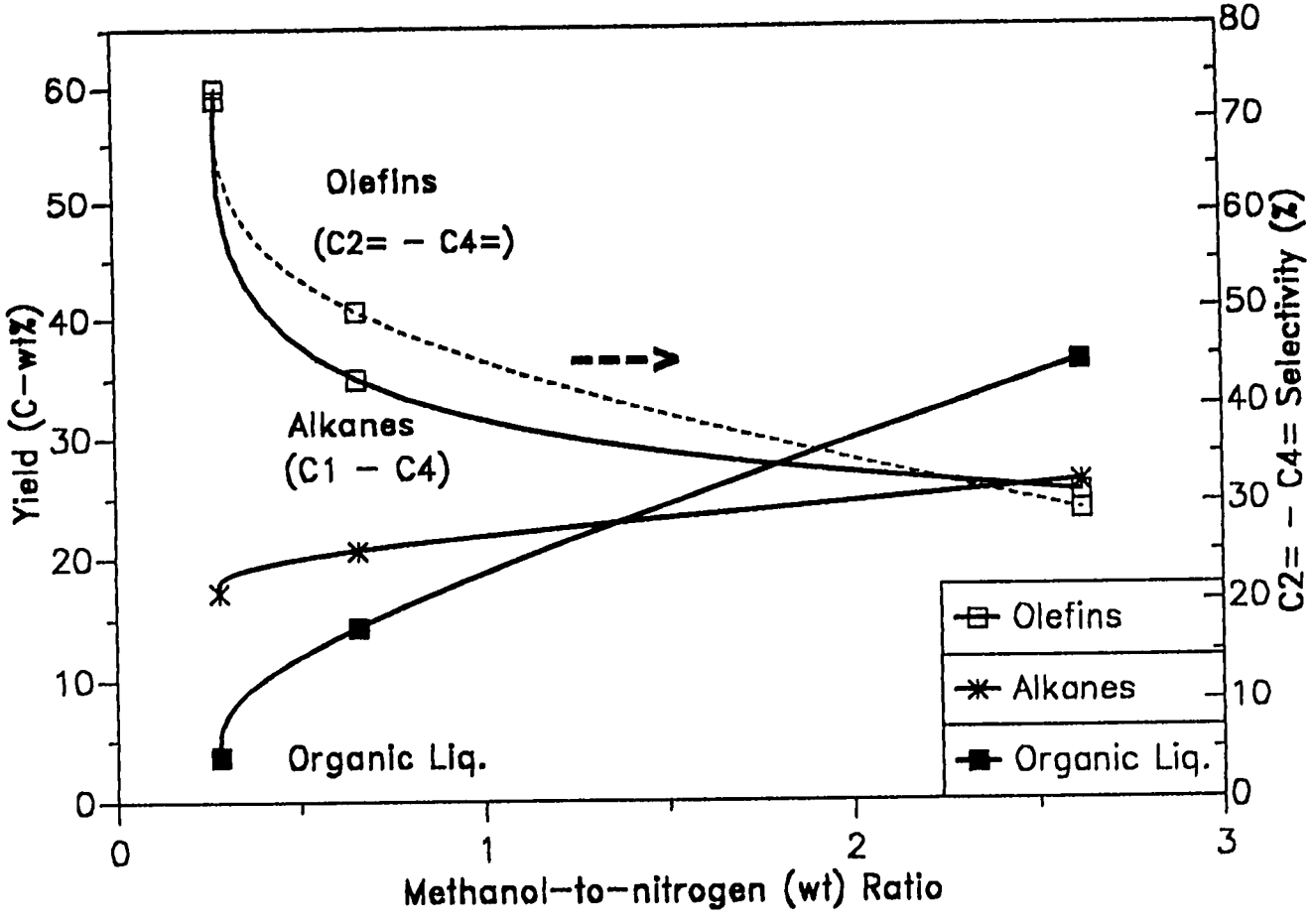


Figure 4.19: Effect of Methanol–to–nitrogen Ratio on Product Distribution for S–115 at 375°C and 4$h^{-1}$ WHSV.

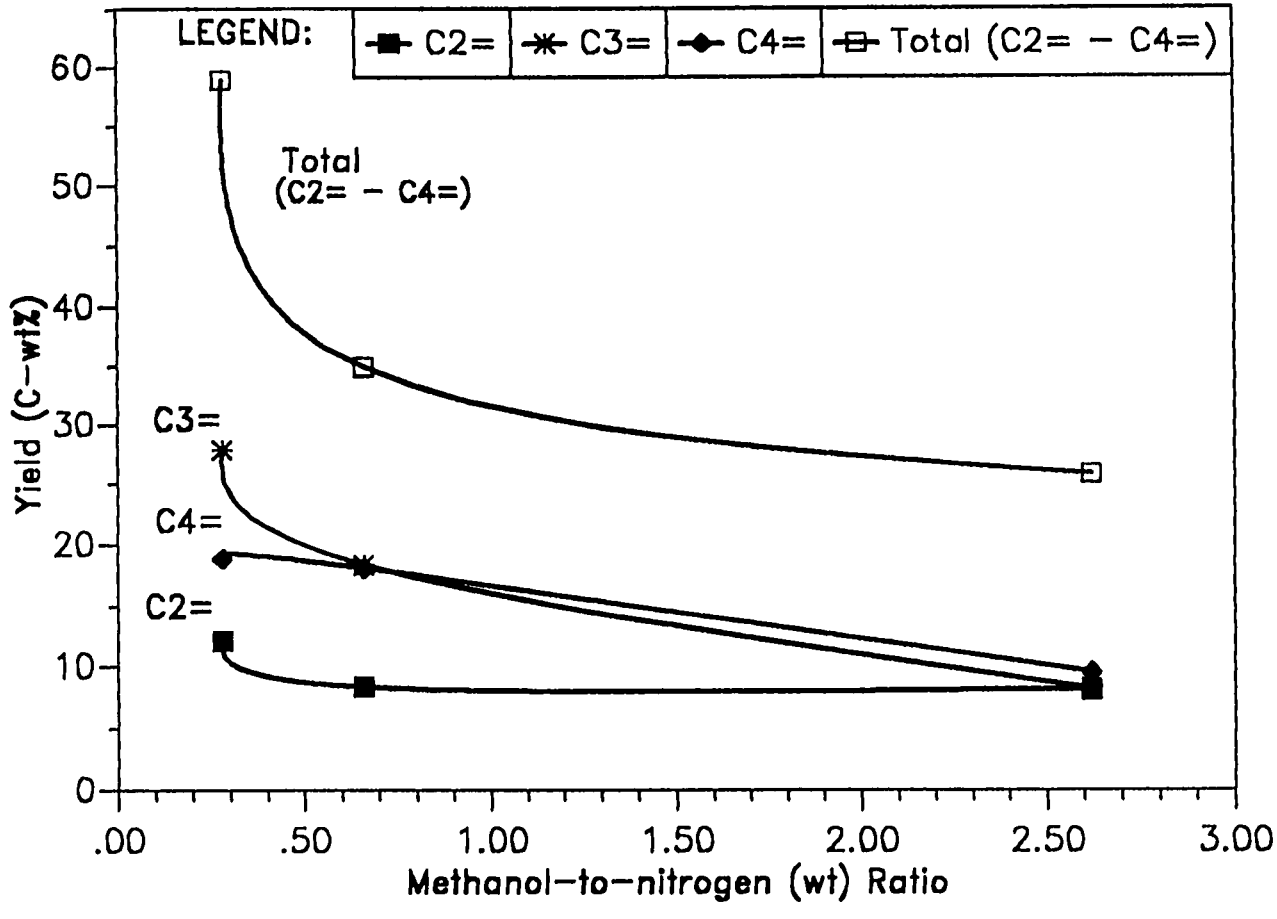


Figure 4.20: Effect of Methanol-to-nitrogen Ratio on Yield of Light Olefins for S-115 at 375°C and $4h^{-1}$ WHSV.

clear trend as function of methanol/nitrogen ratio. These results indicate that for fresh S-115, the optimum methanol/nitrogen wt ratio at 375 °C and $4hr^{-1}$ WHSV is about 0.28.

## 4.4 Extended Studies on Modification of S-115 Catalyst With Barium

Results of screening studies on the effects of various promoters on the activity and selectivity of S-115 in the methanol conversion reaction showed barium to be a good modifier in terms of selectivity to light olefins, life-on-stream as well as coke deposition (section 4.1.2). Additional experiments were conducted employing both impregnation and ion-exchange methods to further investigate the effect of barium loading on the performance of the catalyst in the conversion reaction. The aim was to identify the optimum modification procedure as well as barium loading onto the fresh catalyst. The experimental runs were carried out under optimized process conditions at atmospheric pressure, 375°C, $4hr^{-1}$ WHSV and 2.67 methanol to nitrogen wt ratio.

### 4.4.1. Barium Modification of S-115 by Impregnation

Four different Ba-impregnations of S-115 zeolite were prepared and tested for the methanol conversion reaction. Results of the performance evaluation of the various modifications are given in Table 4.12 and shown graphically in Figures 4.21 - 4.22. The results are presented in terms of product distribution, active life time, coke deposition and average conversion as a function of Ba-loading. Also included are results of the fresh unmodified S-115 representing 0% modification.

Table 4.12 : Effect of Barium Impregnation on Product Distribution for Silicalite S-115 at 375 °C, 4 $hr^{-1}$ WHSV and methanol/nitrogen (wt) ratio of 2.67.

| PARAMETERS | wt % Ba-IMPREGNATION | | | | |
|---|---|---|---|---|---|
| | 0% | 1.25% | 2.8% | 5.2% | 9.8% |
| Total Life-on-stream (h) | 48.0 | 34.5 | 20.3 | 11.5 | 4.5 |
| Life up to DME(h) | 45.0 | 33.3 | 20.3 | 11.5 | 2.0 |
| Coke Dep. Rate (wt %/h) | 0.2 | 0.1 | 0.1 | 0.2 | 1.0 |
| Average Conversion (%) | 98.9 | 98.9 | 97.9 | 98.1 | 95.9 |
| *Light Hydrocarbon Distribution (C-wt%)* | | | | | |
| $C_2^=$ | 8.1 | 6.5 | 10.7 | 9.3 | 4.9 |
| $C_3^=$ | 8.2 | 9.4 | 10.2 | 16.7 | 7.3 |
| $C_4^=$ | 9.5 | 11.7 | 11.6 | 13.5 | 9.0 |
| Total $C_2^= - C_4^=$ Olefins | 25.8 | 27.6 | 32.5 | 39.5 | 21.2 |
| $C_1$ | 1.1 | 1.1 | 0.7 | 1.3 | 0.5 |
| $C_2$ | 0.3 | 0.3 | 0.3 | 0.5 | 0.1 |
| $C_3$ | 4.5 | 2.8 | 3.1 | 2.0 | 2.0 |
| $C_4$ | 11.3 | 7.8 | 7.6 | 4.7 | 5.9 |
| $C_5$ | 8.9 | 5.3 | 5.7 | 3.8 | 5.4 |
| Total $C_1 - C_5$ Alkanes | 26.1 | 17.3 | 17.4 | 12.3 | 13.9 |
| $C_2 - C_4$ Olefin Selectivity(%)* | 29.3 | 36.3 | 50.0 | 54.4 | 34.8 |
| *Product Distribution (C-wt% )* | | | | | |
| Gaseous Hydrocarbons | 51.9 | 44.9 | 49.9 | 51.8 | 35.1 |
| Organic Liquids | 36.2 | 31.1 | 20.8 | 20.8 | 25.9 |
| Other ** | 11.9 | 24.0 | 29.3 | 27.4 | 39.0 |
| Water (g/100g MeOH)*** | 52.9 | 53.3 | 50.1 | 49.8 | 47.3 |

* Selectivity = (Olefins/Total Hydrocarbons)x100

** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether

*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

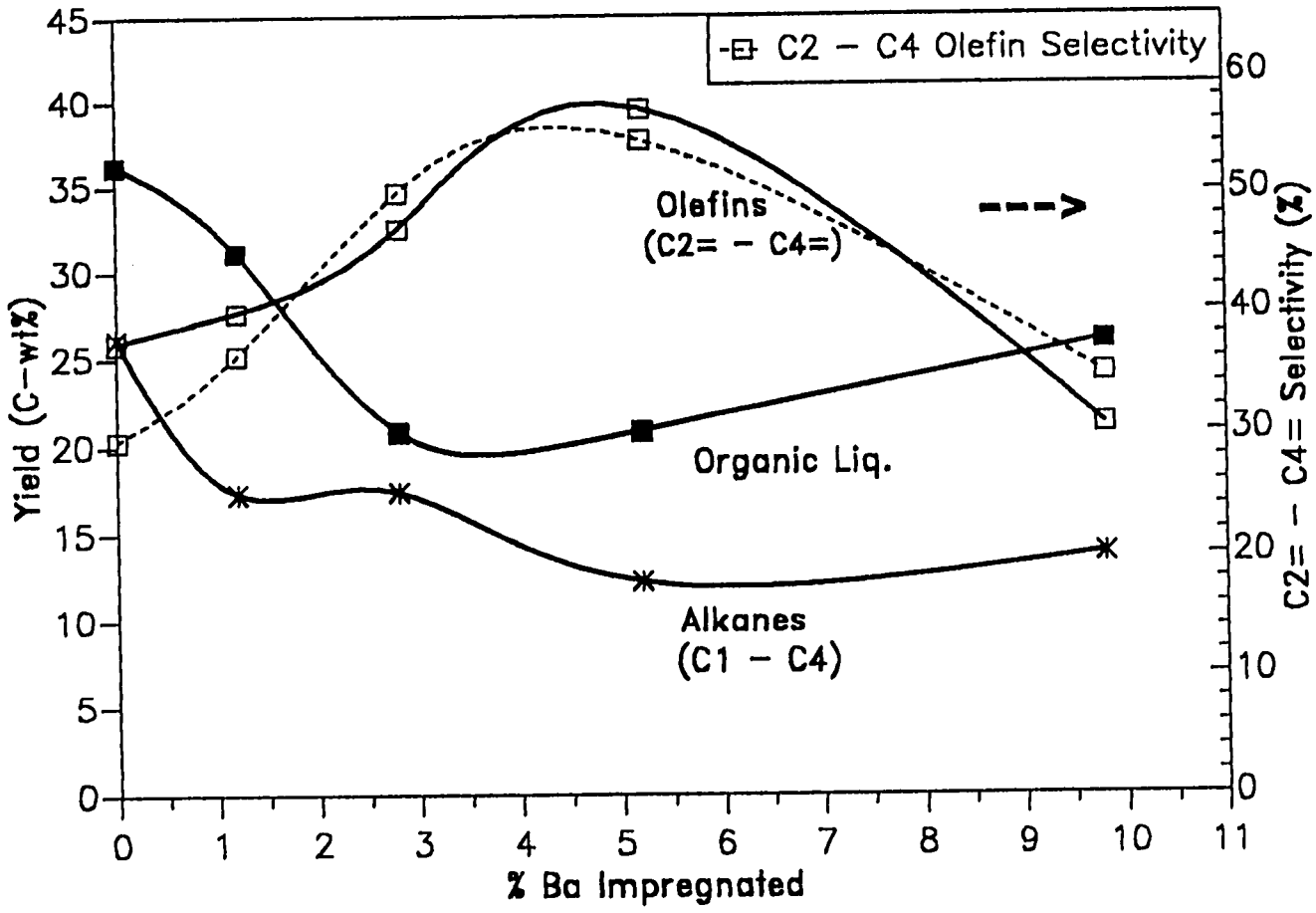


Figure 4.21: Effect of Barium Loading on Product Distribution For S–115 at 375°C, 4$h^{-1}$WHSV and 2.7 Methanol–to–nitrogen (wt) Ratio.

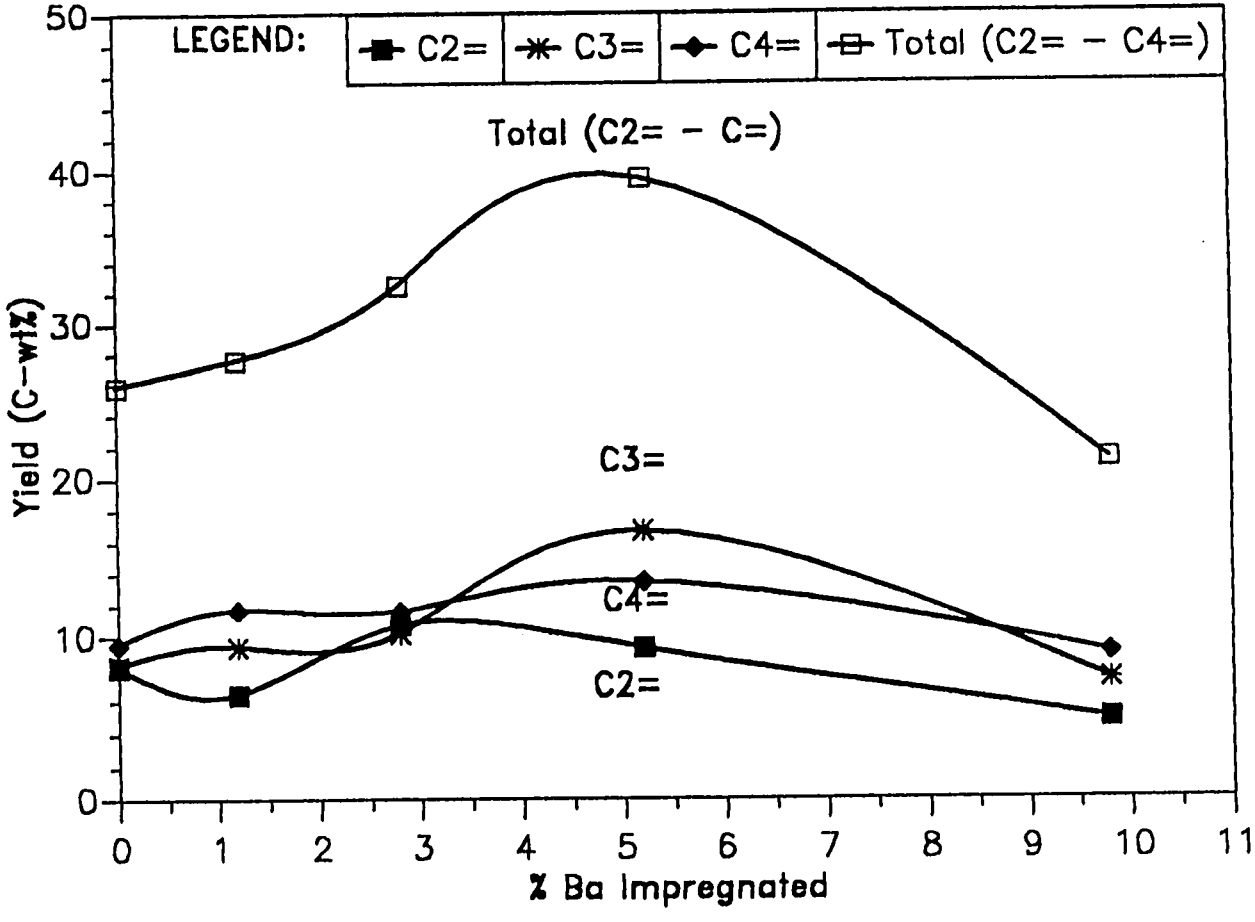


Figure 4.22: Effect of Ba-Loading on Yield of Light Olefins for S-115 at 375 C, 4h WHSV and 2.7 Methanol-to-nitrogen (wt) Ratio.

It can be seen from the table and figures that selectivity to light olefins increased steadily from 29.3% with increase in Ba-loading until a maximum of 54.4% was reached at 5.2% Ba-impregnation. The total $C_2$ - $C_4$olefin yield also exhibited a trend similar to the selectivity with a maximum yield of 39.5% occuring at 5.2% Ba-impregnation. Further increase in Ba-loading led to a decrease in both the yield and selectivity of light olefins. Alkane production however showed an initial decreasing tendency with a minimum occuring at 5.2% Ba-loading before assuming an increasing trend upon further increase in Ba-impregnation. Active lifetime of the zeolite decreased continuously with increasing amount of Ba-loading falling from 45h with fresh S-115 catalyst to only about 2h at 9.8% Ba-loading. Rate of coke deposition decreased initially to a minimum at 1.25% Ba-loading and then increased steadily reaching a maximum of 1.0 wt%/h at 9.8% Ba-impregnation.

Surface area measurements of both fresh and modified catalyst formulations (Table 4.13) showed a slight reduction of about 1.7 - 14.7% with respect to the unmodified S-115 zeolite but with no clear trend as a function of Ba-loading. A notable reduction in pore volume was however brought about by the barium incorporation with variation from 0.83 cc/g to an average of 0.6 cc/g representing a decrease of about 28 %. Similarly a remarkable shift in pore-size distribution was noted with the modified catalysts as compared to the fresh S-115 zeolites (Table 4.13 and Figure 4.23). While the fresh zeolite had pore sizes confined virtually within a narrow range of 1000 - 100000 A, incorporation of Ba into the crystal lattice brought about a wider distribution spectrum with pore sizes ranging from 37 to over 100000 A. Although 85% of pore sizes of the

TABLE 4-13 : Surface Area, Pore Volume and Pore-size Distribution for Fresh and Spent S-115/Ba Modified Catalysts

| CATALYST | Surface Area ($m^2/g$) - | Pore Volume (cc/g) | Pore Size Distribution (Å) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 37 - 100 | 100 - 1000 | 1000 - 10,000 | 10000 - 100,000 | > 100,000 |
| **Fresh Samples** | | | | | | | |
| S-115 | 361 | 0.83 | 0 | 0 | 15 | 85 | 0 |
| S-115/Ba (impregnated) | | | | | | | |
| 1.25% | 355 | 0.62 | 1 | 2 | 41 | 49 | 7 |
| 2.8% | 339 | 0.61 | 1 | 1 | 38 | 53 | 7 |
| 5.2% | 353 | 0.57 | 0 | 1 | 37 | 48 | 14 |
| 9.8% | 308 | 0.60 | 1 | 4 | 35 | 54 | 6 |
| S-115/Ba (Ion-Exchanged) | | | | | | | |
| 0.035% | 352 | 0.63 | 1 | 3 | 43 | 42 | 11 |
| 0.05% | 316 | 0.57 | 1 | 4 | 57 | 32 | 6 |
| 0.03% (Na Route) | 289 | 0.55 | 0 | 3 | 52 | 37 | 8 |
| **Spent Samples** | | | | | | | |
| S-115 | | | | | | | |
| S-115/Ba (impregnated) | | | | | | | |
| 1.25% | 276 | 0.51 | 0 | 0 | 39 | 52 | 8 |
| 2.8% | 257 | 0.48 | 1 | 5 | 42 | 44 | 9 |
| 5.2% | 225 | 0.58 | 3 | 5 | 38 | 47 | 8 |
| 9.8% | 191 | 0.53 | 1 | 3 | 34 | 50 | 9 |
| S-115/Ba (Ion-Exchanged) | | | | | | | |
| 0.035% | 186 | 0.53 | 1 | 4 | 36 | 48 | 12 |
| 0.05% | | | | | | | |
| 0.03% (Na Route) | 260 | 0.51 | 1 | 4 | 44 | 45 | 6 |

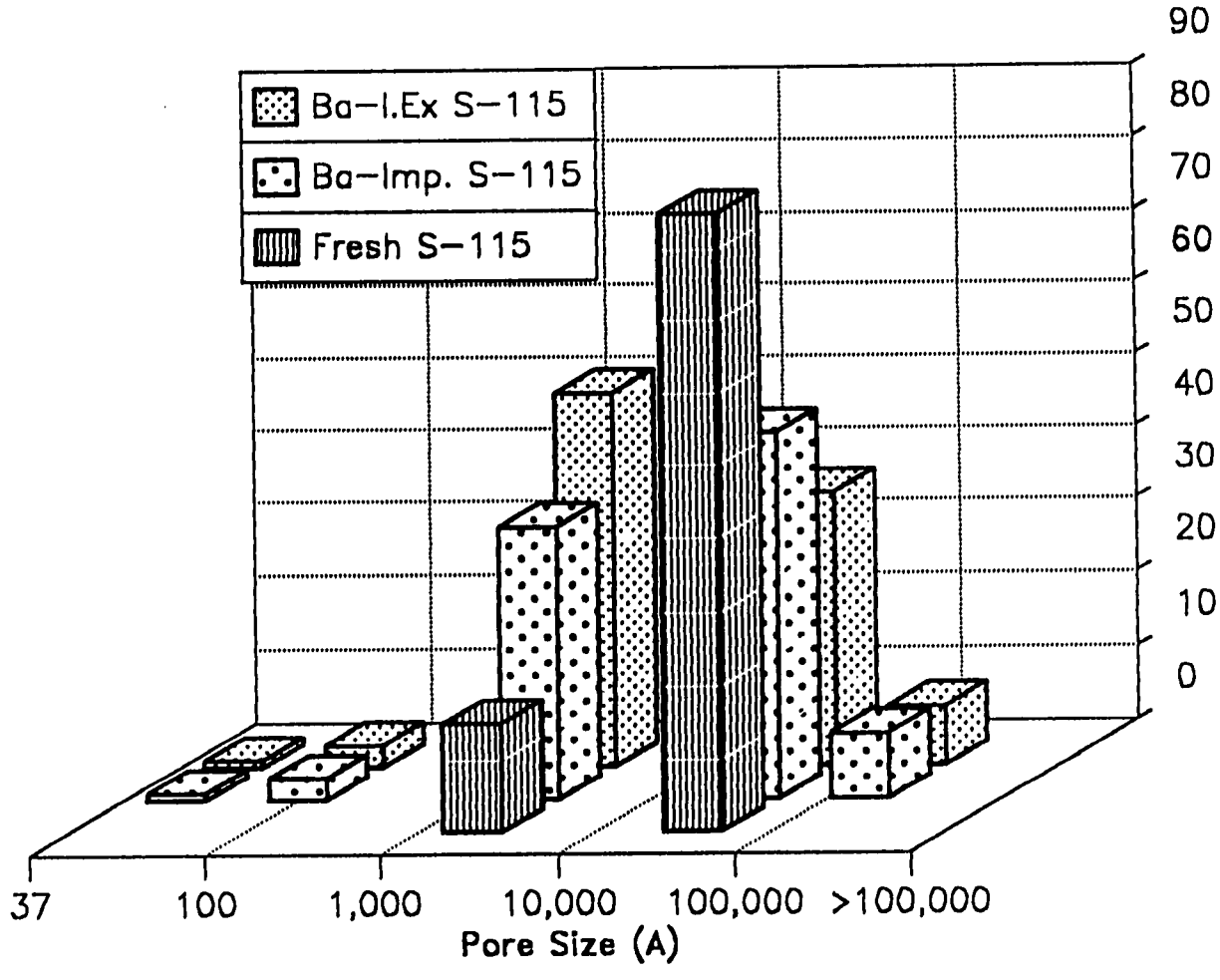


Figure 4.23: Pore-distribution for Fresh and Ba-Modified S-115 Catalyst

fresh S-115 lied within 10000 - 100000 A, only 49% of pores of the modified zeolite fell within this range. Furthermore, 41% of pores of the modified zeolites had sizes within 1000 - 10,000 A as compared to only 15% of the fresh S-115 zeolite. The variation in the pore-size distribution introduced by the Ba incorporation might have had a direct influence in improving the amounts of olefins formed since formation of smaller molecules is in general known to be favoured by narrow pores {13,27}. This might also account for the higher rate of coke formation in the modified zeolites consequently leading to shorter active life-on-stream.

### 4.4.2. Ba-Modification of S-115 by Ion-exchange

Silicalite S-115 was modified with various concentrations of Ba by the ion-exchange procedure described in section 3.5.2. Results of the chemical analysis of the various modified formulations however revealed that only slight degree of ion-exchange was achieved. The highest amount of Ba-loading did not exceed 0.05% of the catalyst. This was attributed to the absence of adequate exchangeable ions (such as sodium) in the zeolite framework structure. The atoms of other elements were present in the zeolite only in trace quantities and most of these elements had electronegativities slightly higher than Barium making them hardly susceptible to ion-exchange by the promoter.

Results of the performance evaluation of the various Ba-modified ion-exchanged catalyst formulations are presented in Table 4.14 and Figures 4.24 - 4.25. It is clear from the table and figures that total yield as well as selectivity to $C_2$ - $C_4$ olefins was improved with 0.03 - 0.04% Ba-ion-exchange. Yields of saturated $C_1$ - $C_5$ alkanes and organic liquids were however slightly lowered for all the modifications. Rate of coke deposition varied between 0.12 and 0.22 wt%/h but without showing a specific trend as a function of Ba-loading.

Surface area measurements as well as results of pore volume and pore-size distribution showed close resemblance to those of barium-impregnated catalysts although the quantities of Ba-loadings for the two cases were significantly different. This suggested that the sites occupied by the incorporated barium

Table 4.14 : Effect of Barium Ion-exchange on Product Distribution for Silicalite S-115 at 375°C, 4 hr $^{-1}$ WHSV and methanol/nitrogen (wt) ratio of 2.67

| PARAMETERS | wt % Ba-Ionexchanged | | | |
|---|---|---|---|---|
| | 0% | 0.03% | 0.04% | 0.05% |
| Total Life-on-stream (h) | 48.0 | 24.0 | 43.0 | 48.0 |
| Life up to DME(h) | 45.0 | 21.5 | < 43.0 | < 48.0 |
| Carbon Deposit (wt%/h) | 0.2 | 0.1 | 0.1 | 0.1 |
| Average Conversion (%) | 98.9 | 93.0 | 93.7 | 91.7 |
| ***Light Hydrocarbon Distribution* (C-wt%)** | | | | |
| $C_2^=$ | 8.1 | 11.4 | 8.4 | 7.5 |
| $C_3^=$ | 8.2 | 12.4 | 12.1 | 8.7 |
| $C_4^=$ | 9.5 | 11.6 | 13.7 | 9.9 |
| **Total $C_2^= - C_4^=$ Olefins** | **25.8** | **35.4** | **34.2** | **26.1** |
| $C_1$ | 1.1 | 0.7 | 1.6 | 1.0 |
| $C_2$ | 0.3 | 0.2 | 0.4 | 0.3 |
| $C_3$ | 4.5 | 3.4 | 4.5 | 4.4 |
| $C_4$ | 11.3 | 9.3 | 11.6 | 10.9 |
| $C_5$ | 8.9 | 7.3 | 7.3 | 7.1 |
| **Total $C_1 - C_5$ Alkanes** | **26.1** | **20.9** | **25.4** | **23.7** |
| **$C_2 - C_4$ Olefin Selectivity(%)*** | **29.3** | **41.3** | **38.1** | **30.9** |
| ***Product Distribution* (C-wt%)** | | | | |
| Gaseous Hydrocarbons | 51.9 | 56.3 | 59.6 | 49.8 |
| Organic Liquids | 36.2 | 29.5 | 30.2 | 34.6 |
| Other ** | 11.9 | 14.2 | 89.8 | 15.6 |
| Water (g/100g MeOH)*** | 52.9 | 46.1 | 47.4 | 45.8 |

* Selectivity = (Olefins/Total Hydrocarbons)x100
** Include $H_2$, $CO_2$, CO, $O_2$, and Dimethylether
*** Water(g/100g MeOH) = (Total water formed(g)/ Total MeOH converted (g))x100

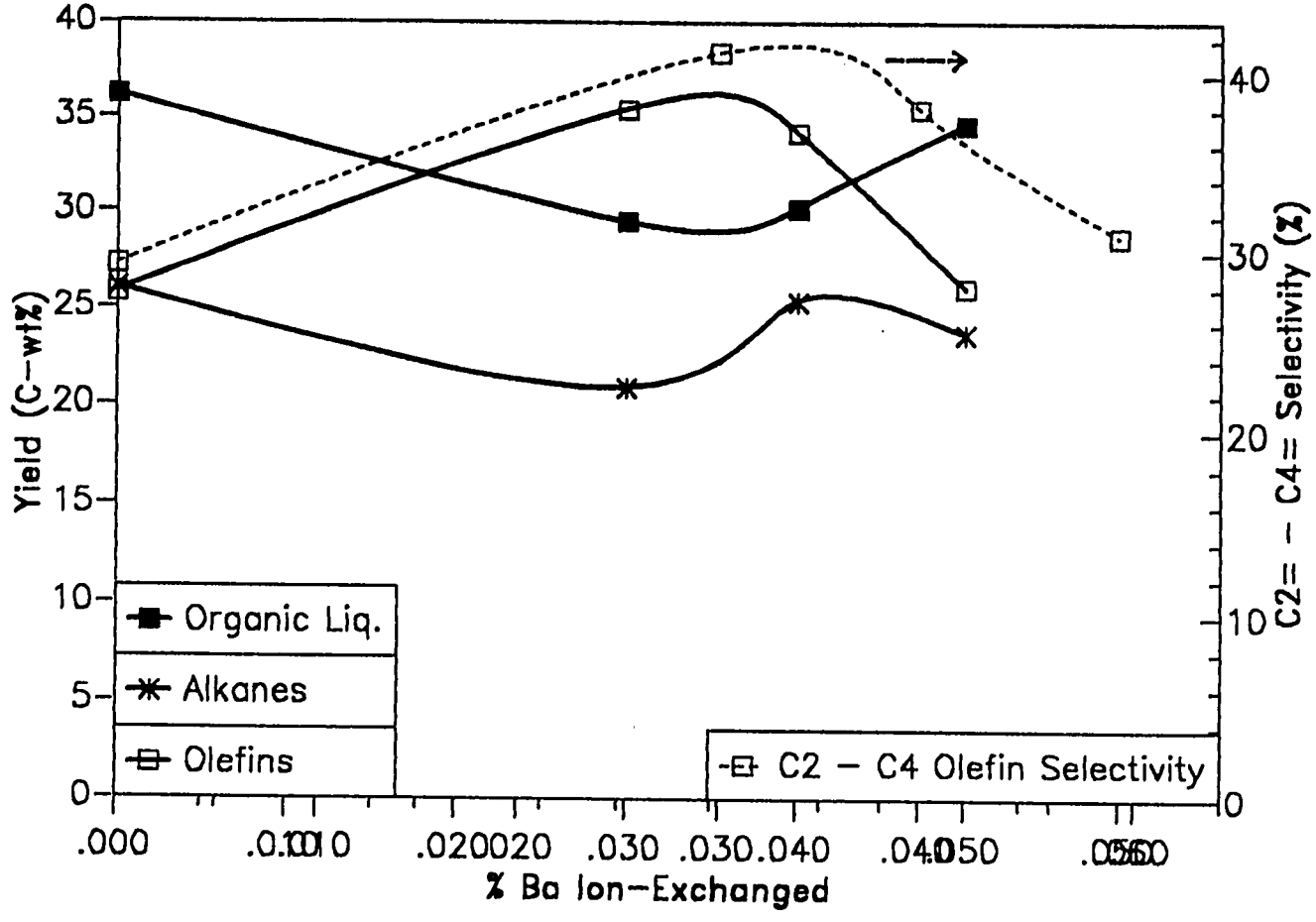


Figure 4.24: Effect of Ba Ion-Exhanged on Product Distribution for S-115 at 375°C, 4h$^{-1}$ WHSV and 2.7 Methanol-to-nitrogen (wt) Ratio.

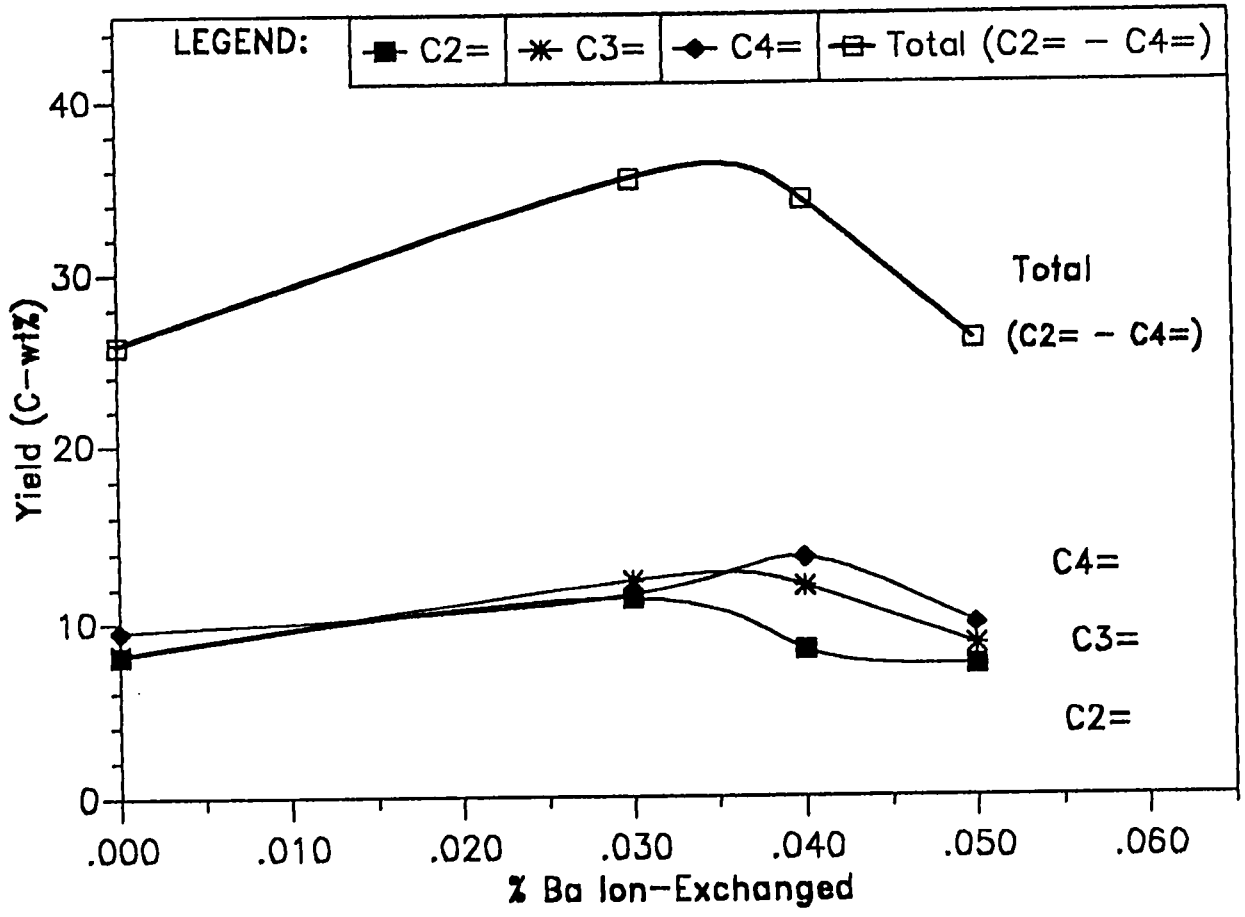


Figure 4.25: Effect of Ba Ion-Exchange on Yield of Light Olefins for S-115 at 375 C, 4h WHSV and 2.7 Methanol-to-nitrogen (wt) Ratio

atoms might be identical for the two modification methods i.e. within channel pores and at inter-lattice spaces rather than within zeolitic framework structure. The higher selectivity of the 0.03% Ba-loaded S-115 may thus be attributed to deactivation of strong acid sites and increased participation of the weak and medium acid centers.

# CHAPTER 5 : CONCLUSIONS AND RECOMMENDATIONS

## *5.1 CONCLUSIONS*

1. Silicalite S-115, ZSM-5 and SAPO-34 are potential zeolites for converting methanol to olefins. However commercial Mordenite, Re-X and US-Y catalysts, did not favor the conversion reaction under fixed bed operating conditions within the ranges of parameters under investigation.

2. ZSM-5 is more selective for production of alkanes and aromatics than olefins. This was attributed mainly to its low silica/alumina ratio. Selectivity to olefins however improved as the catalyst deactivated.

3. Under fixed bed operating conditions in the selected reactor set-up, the optimum temperature for ZSM-5 and S-115 was 450 °C and 375 °C respectively at 4 $hr^{-1}$, and 2.7 methanol-to-nitrogen (wt) ratio.

4. SAPO-34 was not suitable for fixed-bed operation due to high rates of coke formation and short active life-on-stream.

5. Impregnation of ZSM-5 with In, Ag, Cu and Cd affected its product spectrum giving yields of olefins in the order : In > Ag > Cu > Cd. Incorporation of the promoters however lead to a decrease in the active life-on-stream of the catalyst.

6. Impregnation of S-115 with various modifiers brought about a change in the catalyst's activity and selectivity according to the promoter type. Yields of olefins were found to decrease in the order :

Ba > La > Ag > Fresh S-115 > Cu > Ca > Sr > Ga > Cd > In

All modifiers lead to a decrease in the lifetime of the catalyst.

7. The optimum Ba-loading on S-115 in terms of olefin yield and selectivity was 5.2% by impregnation and 0.03% by ion-exchange.

## 5.2 RECOMMENDATIONS FOR FUTURE WORK

1) Results of the performance of S-115 and ZSM-5 indicated that selectivity to light olefins is enhanced by high silica content on a zeolite. It would be interesting to explore synthesis of high silica-containing zeolites of the pentasil type structure and investigate their performance in the methanol conversion reaction.

2) The effect of promoters on the activity and selectivity of zeolites to light olefins might be improved if such promoters were incorporated into the zeolitic framework structure. This could be easily achieved if modification is affected at synthesis stage. Suitable cations that have demonstrated promoting effect in enhancing zeolite selectivity to light olefins such as Ba (as concluded in this study), or Pt, Co and Ti (reported by Inui et al. {56,61}), can be incorporated at the gel formation stage of the synthesis procedure and tested for the MTO conversion.

3) Early deactivation caused by reversible poisoning due to coke deposition is a significant obstacle to a number of zeolites studied in the MTO conversion reaction particularly under fixed-bed operations. This problem might be alleviated through carrying out the reaction using fluidized bed reaction set-up.

4) Results of S-115 modification with various elements on the fifth period of the periodic table indicated that the formation of liquid hydrocarbons in the methanol conversion reaction, might be related to the electronic

configuration of the elements. Additional investigation could be carried out to verify such a possibility.

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# APPENDICES

**TABLE A-1:** List of Elements Screened in Chemical Analysis of Zeolite Samples

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ag | Al | As | As | B | Ba | Be | Bi |
| Ca | Cd | Co | Cu | Cr | Fe | Ge | Hf |
| Hg | In | Ir | K | Li | Mg | Mn | Mo |
| Na | Nb | Ni | P | Re | Pb | Pt | Pd |
| Rh | S | Sb | Si | Sc | Se | Sr | Sn |
| Th | Tl | Te | Ti | V | W | Zn | Zr |

**TABLE A-2 : Chemical Analysis of S-115, ZSM-5 and SAPO-34 Giving Elemental wt%**

| Element | Catalyst | | |
|---|---|---|---|
| | S-115 | ZSM-5 | SAPO-34 |
| Al | 0.29 | 1.67 | 24.53 |
| Bi | 0.02 | - | - |
| Ca | 0.03 | 0.19 | 0.07 |
| Fe | 0.07 | 0.07 | 0.03 |
| Mg | 0.06 | 0.06 | 0.04 |
| Mn | 0.00 | 0.00 | 0.02 |
| Na | 0.04 | 0.03 | 0.07 |
| Ni | 0.00 | 0.00 | 0.03 |
| P | 0.00 | 0.00 | 14.03 |
| Si | 45.31 | 42.71 | 6.37 |
| Ti | 0.02 | 0.30 | 0.00 |
| $SiO_2/Al_2O_3$ | 300 | 48.5 | 0.5 |

**TABLE A-3 :** Surface Area, Pore Volume and Pore-size Distribution of S-115, ZSM-5 and SAPO-34 Catalysts

| CATALYST | Surface Area ($m^2/g$) | Pore Volume (cc/g) | Pore Size Distribution (A) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 37 - 100 | 100 - 1000 | 1000 - 10,000 | 10000 - 100,000 | > 100,000 |
| S-115 | 184 | 0.83 | 0 | 0 | 15 | 85 | 0 |
| ZSM-5 | 318 | 1.73 | 0 | 0 | 28 | 65 | 7 |
| SAPO-34 | 336 | 0.83 | 0 | 0 | 19 | 13 | 68 |

# Appendix A-4

Thermograms of ZSM-5, S-115 and SAPO-34

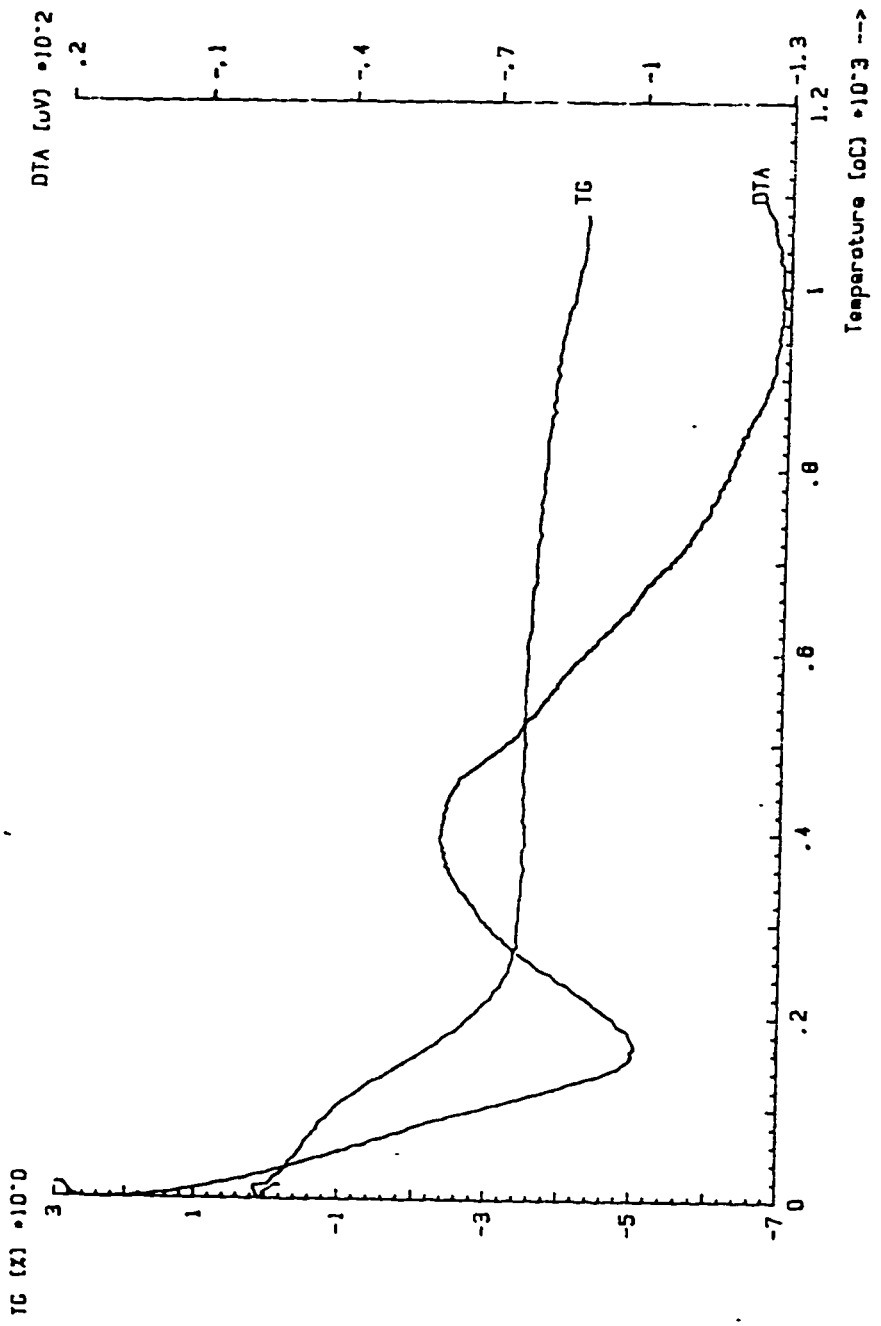



**Figure A4-a :** Thermogram of ZSM-5 Zeolite Sample

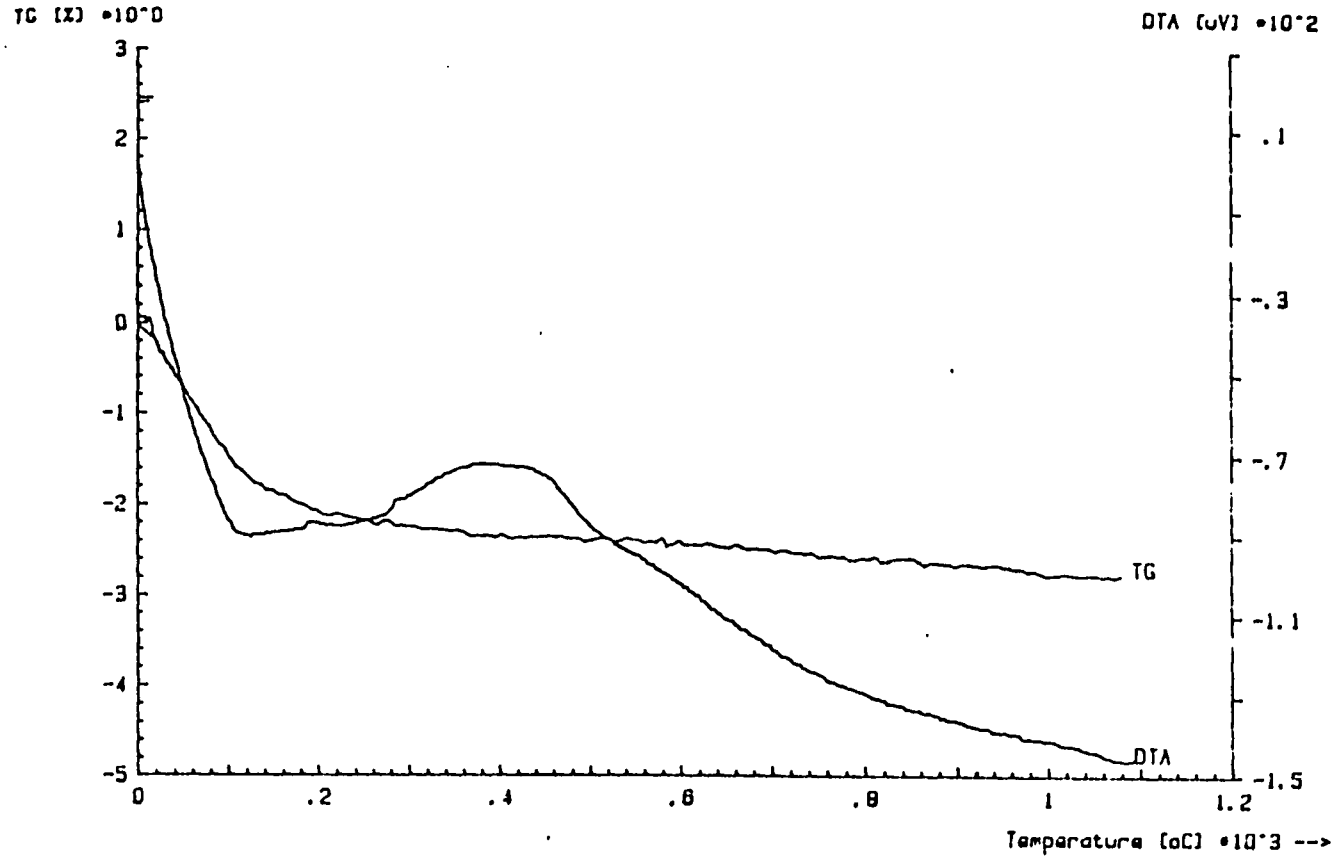



**Figure A4-b :** Thermogram of S-115 Zeolite Sample

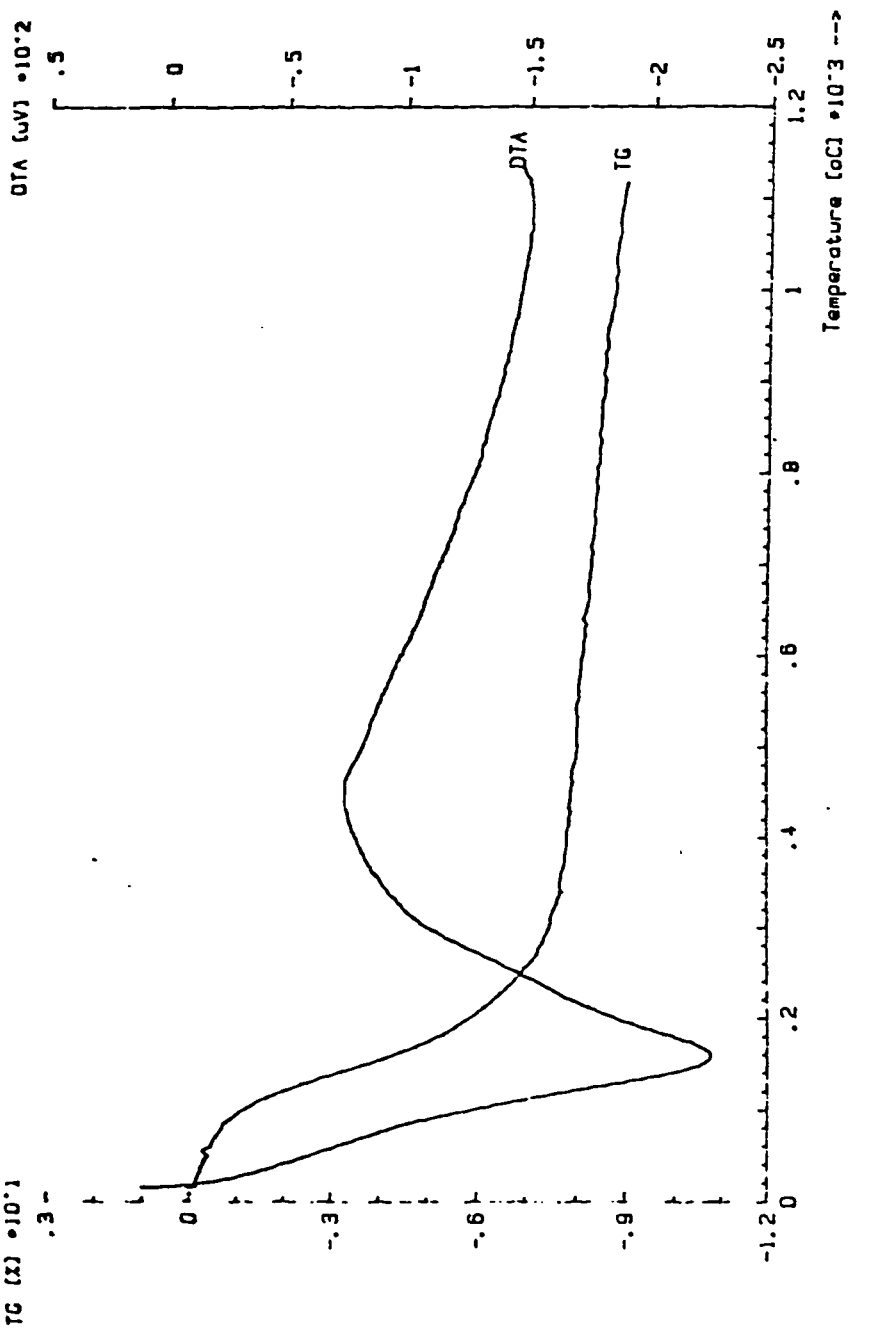



**Figure A4-c :** Thermogram of SAPO-34 Zeolite Sample

**TABLE A-4 :** Characterization Methods and Equipments Used

| ZEOLITE | Temperature of DTA Max. Peak (deg C) | Thermal Effect | Wt. Loss at DTA Peak (%) | Total % Wt. Loss (20-1100C) |
|---|---|---|---|---|
| ZSM-5 | 168 | Endothermic | 3.34 | 4.2 |
| S-115 | 120 | Endothermic | 2.06 | 2.6 |
| SAPO 34 | 158 | Endothermic | 7.60 | 8.0 |

**TABLE A-5 :** Results of XRD and Surface Area for Selected Zeolite Samples

| ZEOLITE | Surface Area ($m^2$ /g) | Degree of Crystallinity |
|---|---|---|
| ZSM-5 | 318 | 100% |
| S-115 | 184 | 95% |
| SAPO 34 | 336 | 85% |

# Appendix A-5

XRD Patterns of ZSM-5, S-115 and SAPO-34

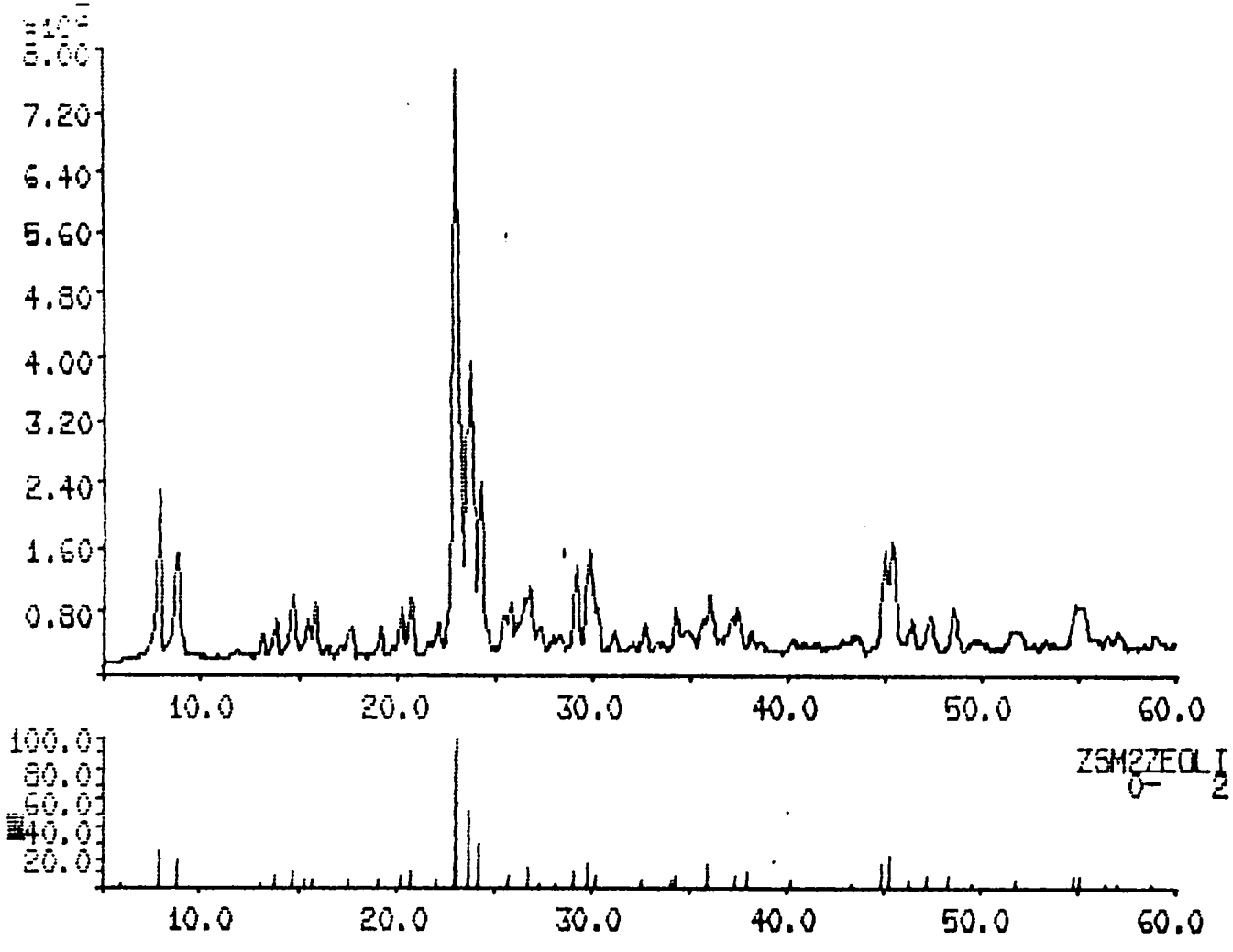



**Figure A5-a :** XRD Pattern of ZSM-5 Zeolite Sample

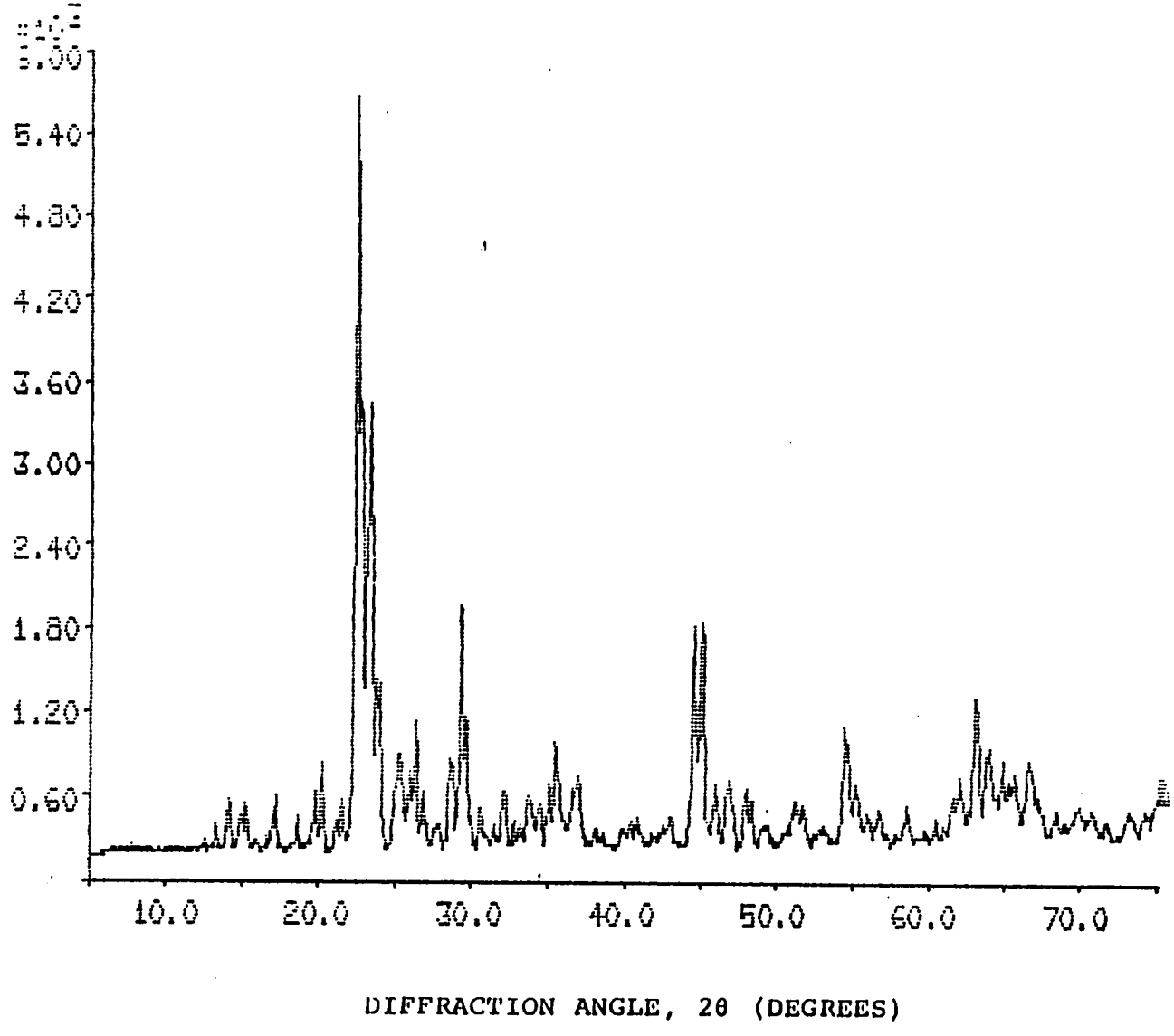



**Figure A5-b :** XRD Pattern of S-115 Zeolite Sample

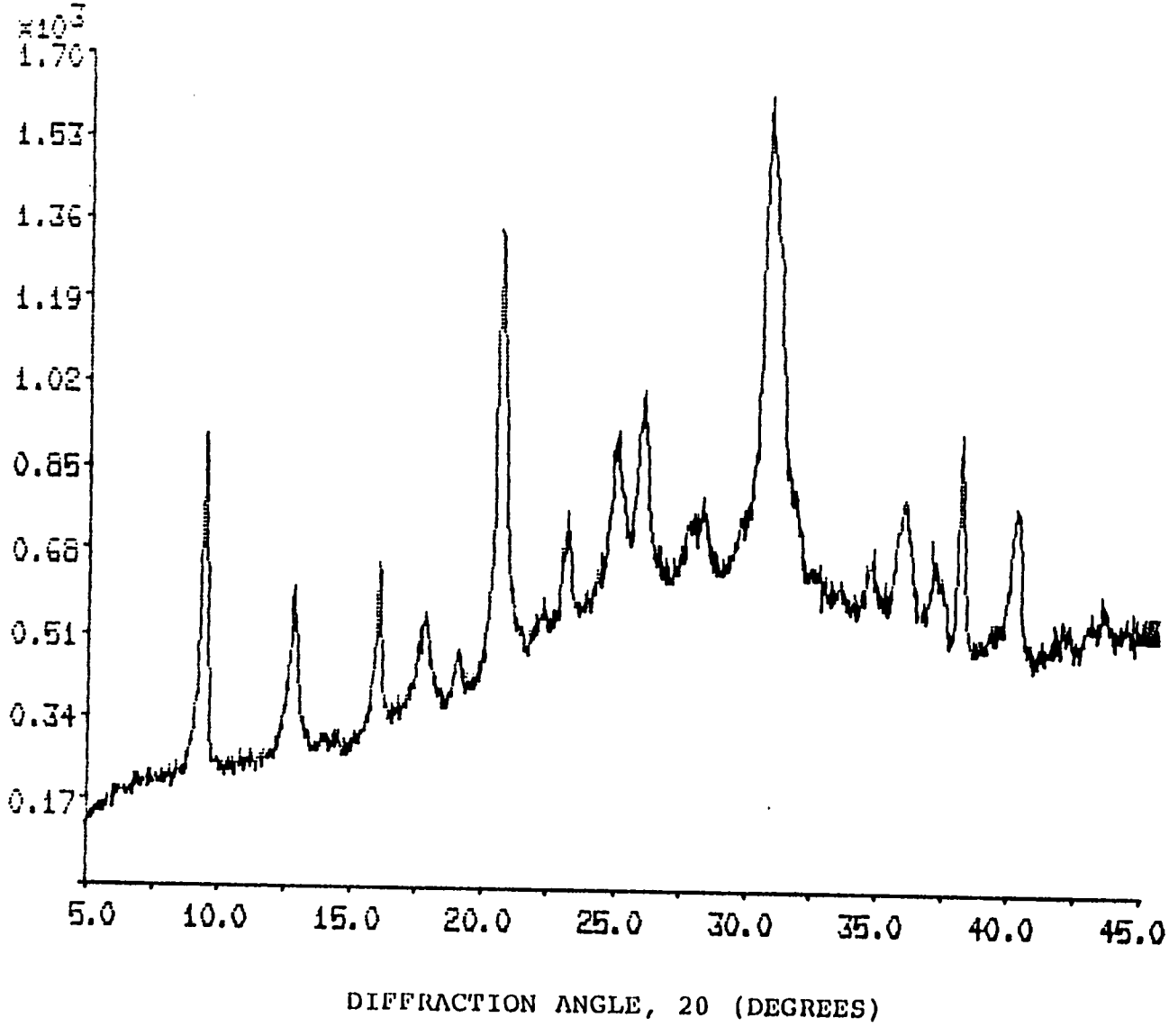
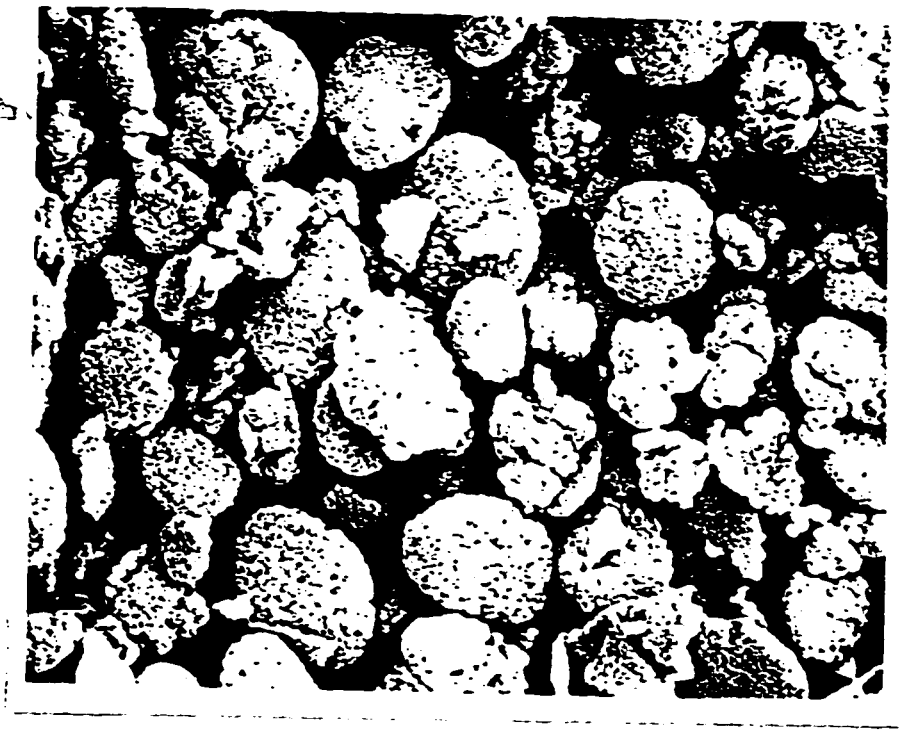



**Figure A5-c :** XRD Pattern of SAPO-34 Zeolite Sample

# Appendix A-6

SEM Micrographs og ZSM-5, S-115 and SAPO-34



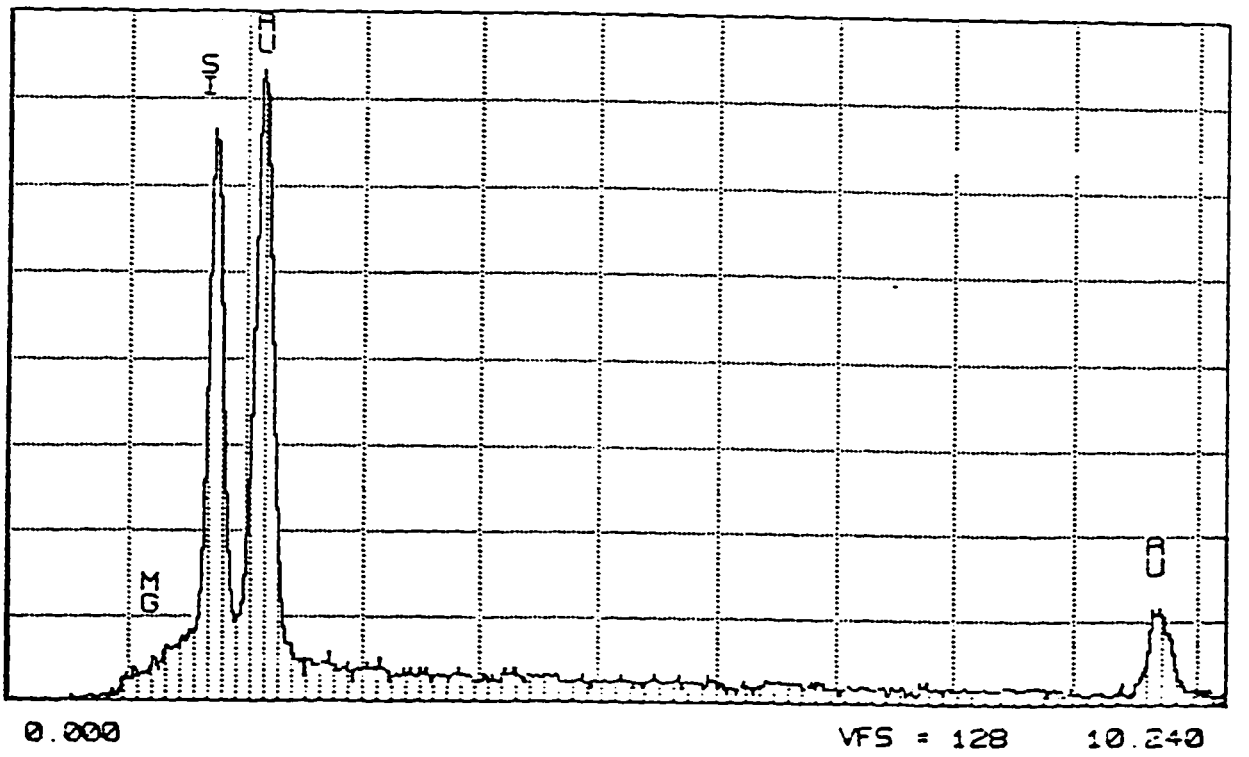
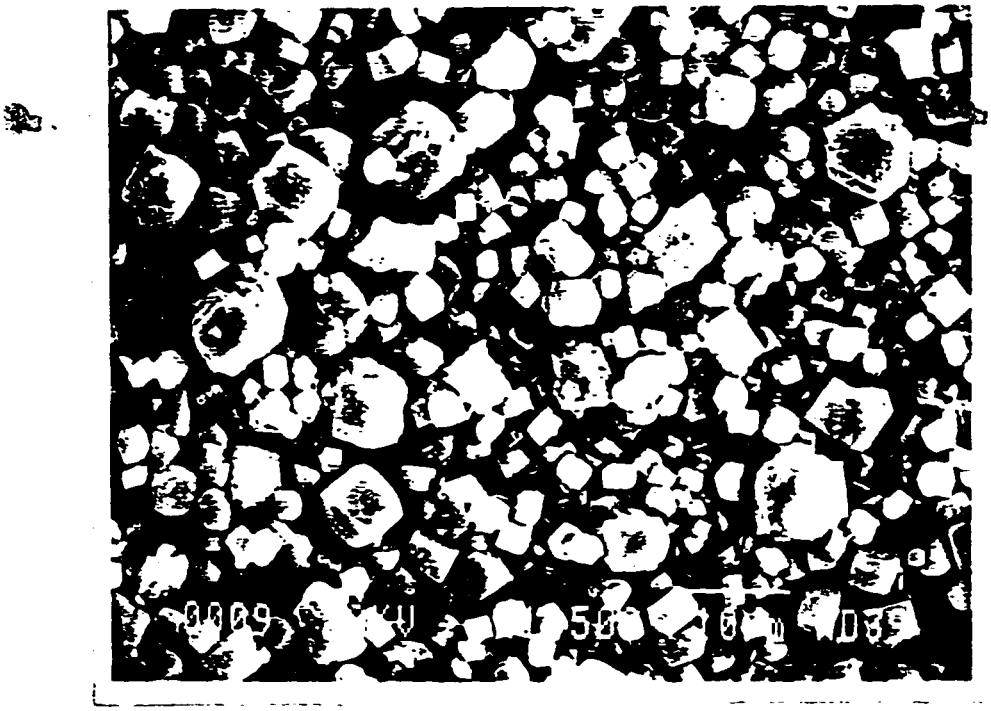



**Figure A6-a :** SEM Micrograph of ZSM-5 Zeolite Sample



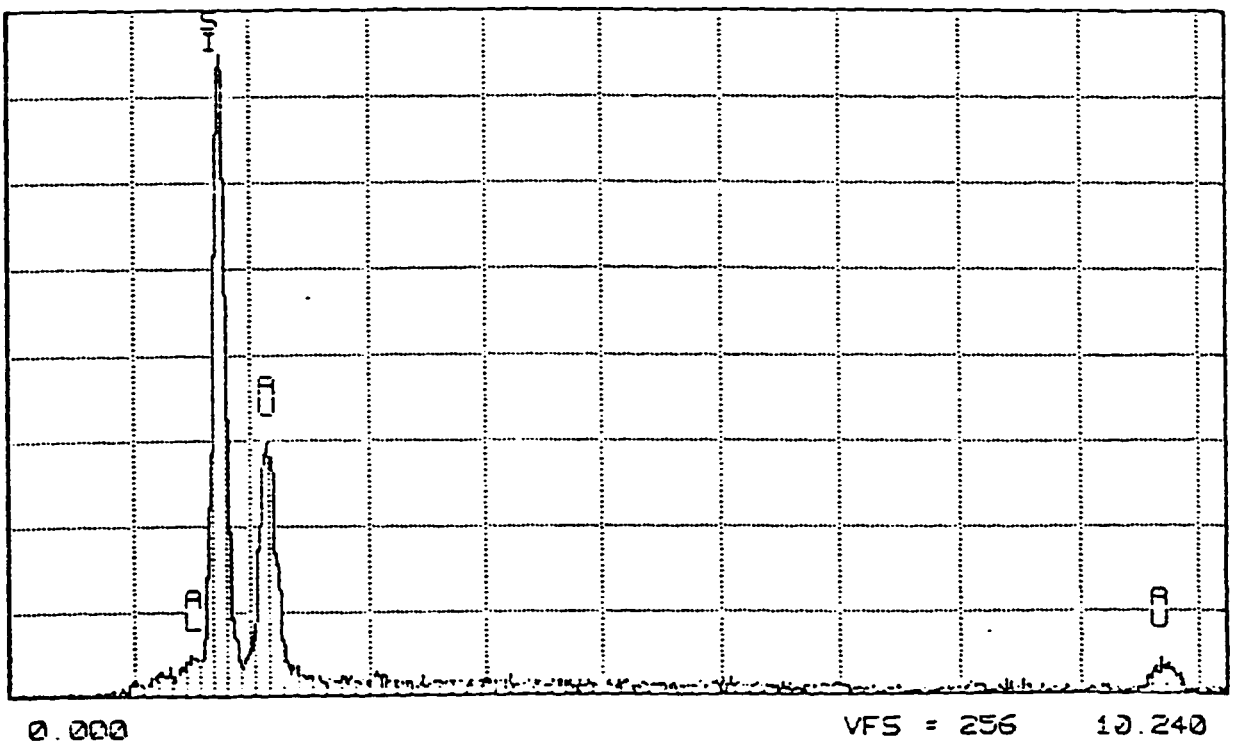
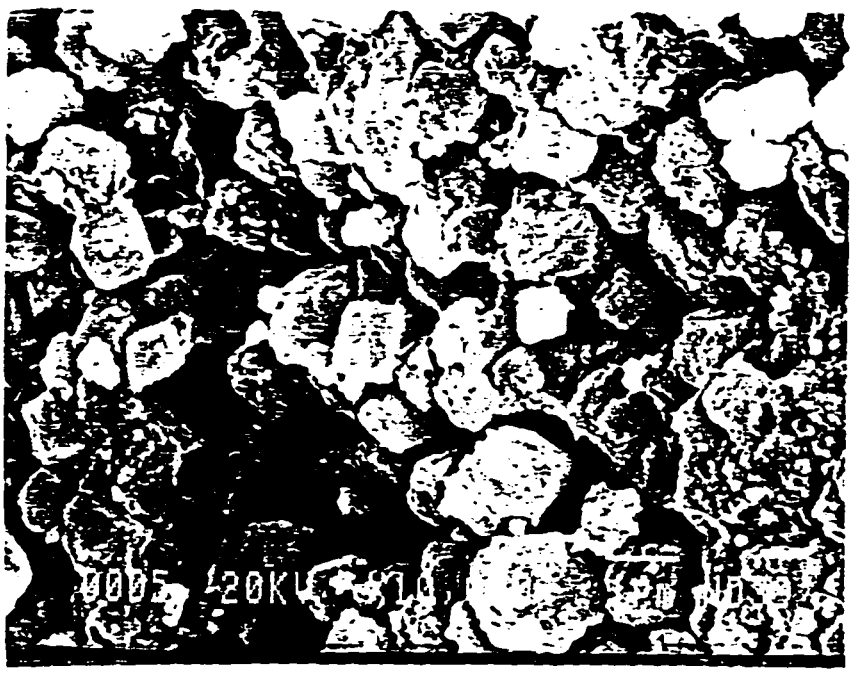



**Figure A6-b :** SEM Micrograph of S-115 Zeolite Sample



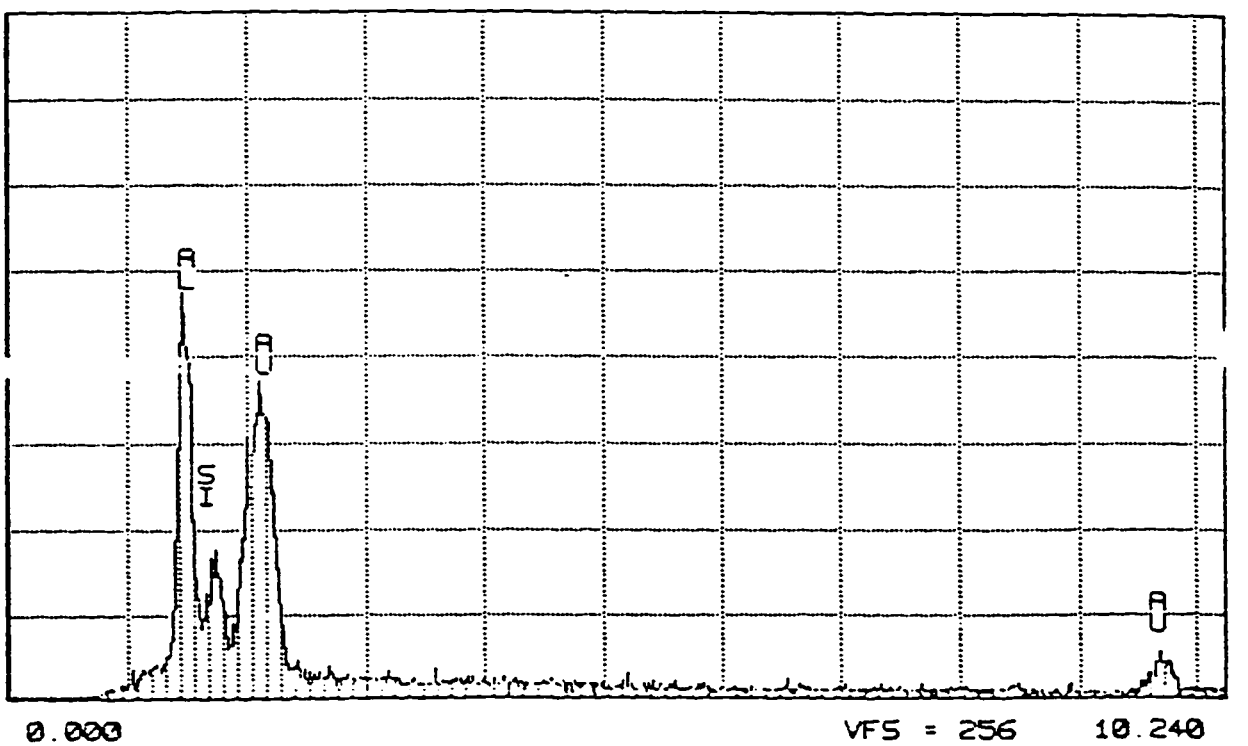



**Figure A6-c :** SEM Micrograph of SAPO-34 Zeolite Sample

## APPENDIX B : Modifications of Various Catalysts (From Literature)

### A. ZSM-5

#### *1. Ion Exchange*

H Mg Ga B B-Al Cr V Sc Ge Mn La
Ni Zr Ti Fe Co Pt Asbestos Th Nb Rh
Ru Zn Na Sr Ca Ba Cs Li Al $NH_4^+$

#### *2. Impregnation*

Mn P Ru Mo Mo-Na Mo-Silicate

#### *3. Synthesis*

Asbestos P Ru Mo Mo-Na Mo-Silicate

### B. HZSM-5

#### *1. Ion Exchange*

Be Tl Nd Pb $NH_4NO_3$ $HNO_3$ $NH_4Cl$ HCl $(NH_4)_2SO_4$
$H_2SO_4$ V V-Cr V-Ru V-Zr Pt Ca

#### *2. Impregnation*

Zn Ce TiK Co Cr Zr AlRh Mg $H_3PO_4$ $Al_2O_3$
$H_3PO_4$-$Al_2O_3$ MgO ZnO CaO $MgO-B_2O_3$ $MgO-P_2O_5$ $ZnO-B_2O_3$
Ni P $CaCO_3$ V

#### *3. Synthesis*

Mg MgO ZnO CaO $MgO-B_2O_3$ $ZnO-B_2O_3$ Ni P $CaCO_3$
V-Cr V-Ru V-Zr

### C. ALPO/SAPO

#### *1. Ion Exchange*

None

#### *2. Impregnation*

None

#### *3. Synthesis*

Li B Ber Mg Si Ti Mn Fe Co Zn Ga Ge
As V H

## APPENDIX C : CACULATION PROCEDURES

Using the results of gas chromatographic analysis of products, the yields of various components of the product mixture was calculated. The yields were evaluated both at sampling points as well as over the whole run, based on total methanol converted. The following procedure were adopted in calculating the yields:

*a). Component yield at sampling points:*

The yield of a component (i) in the product mixture at sampling point is given by :

$$Y_i = \frac{F_i}{F_{MeOH}C} \times 100 \qquad \text{---- (I)}$$

where:

$F_i$ = flowrate of component i (g/h)

$F_{MeOH}$ = flowrate of methanol (g/h)

C = conversion

Since the gases were collected at room temperature and at atmospheric pressure (22°C, and 1 atm ), ideal gas behavior was assumed. Hence for each component,

$$F_i = \frac{273}{295 \times 22.4} \times GM_i x_i$$

$$= 0.0413 GM_i x_i \qquad \text{---- (2)}$$

where:

G = Gaseous product flowrate (l/h)

$M_i$ = Molecular wt of component i

$x_i$ = Volume fraction of component i.

Substituting (2) into (1) gives:

$$Y_i = \frac{0.0413 GM_i x_i}{F_{MeOH} C} \qquad \text{---- (3)}$$

***b). Overall Component Yield:***

The overall yield of a component $Y_{io}$ over the whole run, was evaluated by integrating the total area under the $F_i$ versus time curve using the trapezoidal rule.

Applying the trapezoidal rule, the overall yield is given by:

$$Y_{io} = \frac{\sum_{j=0}^{n} \frac{1}{2}(F_j + F_{j-1})\Delta T_j}{CF_{MeOH}\sum_{j=0}^{n}\Delta T_j} \times 100 \qquad \text{---- (4)}$$

where :

$Y_{io}$ = Total yield of component i (g/100g MeOH)

$\Delta T_j$ = Sampling time interval (h)

j = Sampling number

n = Sample number at which DME appears

*c). Yield based on carbon:*

The yields of various components in the product mixture were also calculated based on the carbon fed. This was adopted for two reasons:

1. The products of interests are produced only from the carbon and some of the hydrogen of the methanol initially fed as the main reactant.

2. Material balance on carbon provides a better account of other non-detectable hydrocarbons that might have been produced.

The yield of a component based on carbon is defined as follows:

$$\psi_i = \frac{\text{total C converted to i}}{\text{total C fed in MeOH}} \qquad \text{---- (5)}$$

where $\psi_i$ = % C yield in component i

From equation (4), the % yield of a component was expressed in g of the component produced per 100g of methanol converted. Hence

$$\psi_i = \frac{\text{g Carbon in component i}}{\text{g Carbon in 100g sub MeOH Converted}}$$

or,

$$\psi_i = Y_{io} \times \frac{a_i}{a_{MeOH}} \times 100$$

$$= 100 Y_{io} \gamma \qquad \text{---- (6)}$$

where

$a_i$ = %C in a molecule of component i

$a_{MeOH}$ = %C in a molecule of MeOH and

$$\gamma = \frac{a_i}{a_{MeOH}}$$

Thus the yield of each component based on carbon fed can be determined from the component overall yield and vice versa. Table B-1 gives values of the a's and $\gamma$'s used in calculating the carbon-based yields of the various components.

**TABLE C-1 :** Parameters for equation (6) used in calculating Carbon-based yields of various components in the product mixture.

| Component | Molecular wt | a | γ |
|---|---|---|---|
| $CH_3OH$ | 32 | 37.5 | 1 |
| $C_2H_4$ | 28 | 85.7 | 2.3 |
| $C_3H_6$ | 42 | 85.7 | 2.3 |
| $C_4H_8$ | 56 | 85.7 | 2.3 |
| $CH_4$ | 16 | 75.0 | 2.0 |
| $C_2H_6$ | 30 | 80.0 | 2.1 |
| $C_3H_8$ | 44 | 81.8 | 2.2 |
| $C_4H_{10}$ | 58 | 82.8 | 2.2 |
| $C_5H_{12}$ | 72 | 83.3 | 2.2 |
| $C_6^+$* | n(14) | 85.7 | 2.3 |

* Average formula for $C_6^+$ organic liquids is $n(CH_2)$ with $n > 6$

**Table C-2 :** Reproducibility Runs at 400 °C Using S-115 Catalyst (WHSV = 4 $h^{-1}$ ; Methanol-to-Nitrogen (wt) Ratio = 2.67).

| PARAMETERS | Run-1 | Run-2 | Average | % Dev. |
|---|---|---|---|---|
| **Average Conversion (%)** | 98.4 | 97.8 | 98.1 | 0.3 |
| ***Product Distribution (wt% Yield )*** | | | | |
| **Water** | 53.1 | 52.9 | 53.0 | 0.2 |
| **Organic Liquids** | 15.1 | 15.2 | 15.2 | 0.7 |
| **Gaseous Hydrocarbons** | 22.9 | 22.3 | 22.6 | 1.3 |
| ***Light Hydrocarbon Distribution (wt%)*** | | | | |
| $C_2^-$ | 2.8 | 3.4 | 3.1 | 9.7 |
| $C_3^-$ | 4.0 | 3.8 | 3.9 | 2.6 |
| $C_4^-$ | 4.7 | 3.9 | 4.3 | 9.3 |
| **Total $C_2^-$ – $C_4^-$ Olefins** | **11.5** | **11.1** | **11.3** | **1.8** |
| $C_1$ | 0.9 | 0.2 | 0.6 | 66.7 |
| $C_2$ | 0.2 | 0.1 | 0.2 | 50.0 |
| $C_3$ | 2.0 | 2.0 | 2.0 | 0.0 |
| $C_4$ | 4.8 | 4.9 | 4.9 | 2.0 |
| $C_5$ | 3.5 | 4.0 | 3.8 | 5.3 |
| **Total $C_1$ – $C_5$ Alkanes** | **11.4** | **11.2** | **11.3** | **0.9** |

**Table C-3 :** Reproducibility Runs at 375 ° C, Using S-115 Catalyst (WHSV = 4 h ; Methanol-to-Nitrogen (wt) Ratio = 2.67).

| PARAMETERS | Run-1 | Run-2 | Average | % Dev. |
|---|---|---|---|---|
| **Average Conversion (%)** | 92.3 | 94.5 | 93.4 | 1.2 |
| ***Product Distribution*** *(wt% Yield )* | | | | |
| **Water** | 51.1 | 52.5 | 51.8 | 1.4 |
| **Organic Liquids** | 11.1 | 12.1 | 11.6 | 4.3 |
| **Gaseous Hydrocarbons** | 35.2 | 34.4 | 34.8 | 1.1 |
| ***Light Hydrocarbon Distribution*** *(wt% C)* | | | | |
| $C_2^-$ | 2.0 | 1.9 | 2.0 | 5.0 |
| $C_3^-$ | 5.0 | 6.4 | 5.7 | 12.3 |
| $C_4^-$ | 9.6 | 8.3 | 9.0 | 3.3 |
| **Total $C_2^-$ – $C_4^-$ Olefins** | **16.6** | **16.6** | **16.6** | **0.0** |
| $C_1$ | 0.5 | 0.8 | 0.7 | 28.6 |
| $C_2$ | 0.2 | 0.3 | 0.3 | 33.3 |
| $C_3$ | 2.5 | 3.0 | 2.8 | 10.7 |
| $C_4$ | 6.5 | 6.4 | 6.5 | 1.5 |
| $C_5$ | 8.9 | 7.3 | 8.1 | 11.0 |
| **Total $C_1$ – $C_5$ Alkanes** | **18.6** | **17.8** | **18.2** | **2.3** |

```
C                                                                       PRG00010
C***********************************************************************C PRG00020
C                                                                       C PRG00030
C                                                                       C PRG00040
C                                                                       C PRG00050
C********     COMPUTER PROGRAM USED FOR DATA ANALYSIS          **********C PRG00060
C********          USING TRAPEZOIDAL RULE                      **********C PRG00070
C                                                                       C PRG00080
C                                                                       C PRG00090
C***********************************************************************C PRG00100
C                                                                       PRG00110
C                                                                       PRG00120
C                                                                       PRG00130
C                                                                       PRG00140
      IMPLICIT REAL*8(A-H,O-Z)                                          PRG00150
      DIMENSION NSAMPL(0:90),TIME(0:90),GSRATE(0:90),C1(0:90),          PRG00160
     +C1Y(0:90),C2(0:90),C2Y(0:90),C22(0:90),C22Y(0:90),C3(0:90),       PRG00170
     +C3Y(0:90),C33(0:90),C33Y(0:90),C4(0:90),C4Y(0:90),C44(0:90),      PRG00180
     +C44Y(0:90),C5(0:90),C5Y(0:90),C1F(0:90),C2F(0:90),C22F(0:90),     PRG00190
     +C3F(0:90),C33F(0:90),C4F(0:90),C44F(0:90),C5F(0:90),TOTALK(0:90), PRG00200
     +TOTOLE(0:90),ALKNS(0:90),OLFNS(0:90)                              PRG00210
C                                                                       PRG00220
      DATA FMEOH,GASRT,TEMP,WHSV,N,M /19.9,9.84,450.,4.0,6,5/           PRG00230
      G=GASRT                                                           PRG00240
C                                                                       PRG00250
C  CLEAR ZERO ARRAY                                                     PRG00260
C                                                                       PRG00270
      TIME(0)=0.                                                        PRG00280
      C1(0)=0.                                                          PRG00290
      C2(0)=0.                                                          PRG00300
      C22(0)=0.                                                         PRG00310
      C3(0)=0.                                                          PRG00320
      C33(0)=0.                                                         PRG00330
      C4(0)=0.                                                          PRG00340
      C44(0)=0.                                                         PRG00350
      C5(0)=0.                                                          PRG00360
C                                                                       PRG00370
C   READ IN DATA                                                        PRG00380
C                                                                       PRG00390
      READ(3,*) FC1,FC2,FC22,FC3,FC33,FC4,FC44,FC5                      PRG00400
C                                                                       PRG00410
      DO 10 I=1,N                                                       PRG00420
      NSAMPL(I)=I                                                       PRG00430
      READ (4,*) TIME(I),C22(I),C33(I),C44(I),C1(I),C2(I),C3(I),        PRG00440
     +C4(I),C5(I)                                                       PRG00450
      ALKNS(I)=C1(I)+C2(I)+C3(I)+C4(I)+C5(I)                            PRG00460
      OLFNS(I)=C22(I)+C33(I)+C44(I)                                     PRG00470
   10 CONTINUE                                                          PRG00480
C                                                                       PRG00490
C                                                                       PRG00500
C    WRITE HEADINGS   AND INPUT DATA                                    PRG00510
C                                                                       PRG00520
C     WRITE(1,99) TEMP,WHSV,TIME(N)                                     PRG00530
C     WRITE(2,99) TEMP,WHSV,TIME(N)                                     PRG00540
C     WRITE(5,99) TEMP,WHSV,TIME(N)                                     PRG00550
```

```
      WRITE(6,99) TEMP,WHSV,TIME(N)                                     PRG00560
C     WRITE(7,99) TEMP,WHSV,TIME(N)                                     PRG00570
C     WRITE(8,99) TEMP,WHSV,TIME(N)                                     PRG00580
      WRITE(10,99)TEMP,WHSV,TIME(N)                                     PRG00590
      WRITE(11,99)TEMP,WHSV,TIME(N)                                     PRG00600
C     WRITE(1,715)                                                      PRG00610
C     WRITE(1,730)                                                      PRG00620
C     WRITE(2,720)                                                      PRG00630
C     WRITE(2,740)                                                      PRG00640
C     WRITE(7,103)                                                      PRG00650
C     WRITE(7,110)                                                      PRG00660
C     WRITE(8,105)                                                      PRG00670
C     WRITE(8,120)                                                      PRG00680
      WRITE(10,100)                                                     PRG00690
      WRITE(10,747)                                                     PRG00700
      WRITE(11,710)                                                     PRG00710
      WRITE(11,747)                                                     PRG00720
      WRITE(6,150) GASRT                                                PRG00730
C                                                                       PRG00740
C                                                                       PRG00750
      DO 15 I=1,N                                                       PRG00760
C     WRITE(7,130) NSAMPL(I),TIME(I),C22(I),C33(I),C44(I)               PRG00770
C     WRITE(8,140) NSAMPL(I),TIME(I),C1(I),C2(I),C3(I),C4(I),C5(I)      PRG00780
      WRITE(10,135) NSAMPL(I),TIME(I),C22(I),C33(I),C44(I),             PRG00790
     +C1(I),C2(I),C3(I),C4(I),C5(I),OLFNS(I),ALKNS(I)                   PRG00800
   15 CONTINUE                                                          PRG00810
C                                                                       PRG00820
C   POINT MASS-FLOWRATE                                                 PRG00830
C                                                                       PRG00840
C     WRITE(6,350)                                                      PRG00850
                                                                        PRG00860
      DO 20 I=0,N                                                       PRG00870
      C1F(I)  = C1(I)*FC1*G                                             PRG00880
      C2F(I)  = C2(I)*FC2*G                                             PRG00890
      C22F(I) = C22(I)*FC22*G                                           PRG00900
      C3F(I)  = C3(I)*FC3*G                                             PRG00910
      C33F(I) = C33(I)*FC33*G                                           PRG00920
      C4F(I)  = C4(I)*FC4*G                                             PRG00930
      C44F(I) = C44(I)*FC44*G                                           PRG00940
      C5F(I)  = C5(I)*FC5*G                                             PRG00950
C                                                                       PRG00960
C     POINT YIELD                                                       PRG00970
C                                                                       PRG00980
      C1Y(I)  = C1F(I)*100./FMEOH                                       PRG00990
      C2Y(I)  = C2F(I)*100./FMEOH                                       PRG01000
      C22Y(I) = C22F(I)*100./FMEOH                                      PRG01010
      C3Y(I)  = C3F(I)*100./FMEOH                                       PRG01020
      C33Y(I) = C33F(I)*100./FMEOH                                      PRG01030
      C4Y(I)  = C4F(I)*100./FMEOH                                       PRG01040
      C44Y(I) = C44F(I)*100./FMEOH                                      PRG01050
      C5Y(I)  = C5F(I)*100./FMEOH                                       PRG01060
      TOTOLE(I)=C22Y(I)+C33Y(I)+C44Y(I)                                 PRG01070
      TOTALK(I)=C1Y(I)+C2Y(I)+C3Y(I)+C4Y(I)+C5Y(I)                      PRG01080
      IF(I.EQ.0) GO TO 20                                               PRG01090
      WRITE(5,300) TIME(I),TOTOLE(I),TOTALK(I)                          PRG01100
```

```
C      WRITE(2,700) NSAMPL(I),TIME(I),C1Y(I),C2Y(I),C3Y(I),C4Y(I),          PRG01110
C     +C5Y(I),TOTALK(I)                                                     PRG01120
       WRITE(11,135) NSAMPL(I),TIME(I),C22Y(I),C33Y(I),C44Y(I),             PRG01130
      +C1Y(I),C2Y(I),C3Y(I),C4Y(I),C5Y(I),TOTOLE(I),TOTALK(I)               PRG01140
  20  CONTINUE                                                              PRG01150
      WRITE(5,748)                                                          PRG01160
      WRITE(5,99) TEMP,WHSV,TIME(N)                                         PRG01170
C                                                                           PRG01180
C   INTEGRATION SECTION                                                     PRG01190
C                                                                           PRG01200
C   CLEAR INTEGRALS                                                         PRG01210
C                                                                           PRG01220
      SUMC1  = 0.0                                                          PRG01230
      SUMC2  = 0.0                                                          PRG01240
      SUMC22 = 0.0                                                          PRG01250
      SUMC3  = 0.0                                                          PRG01260
      SUMC33 = 0.0                                                          PRG01270
      SUMC4  = 0.0                                                          PRG01280
      SUMC44 = 0.0                                                          PRG01290
      SUMC5  = 0.0                                                          PRG01300
C                                                                           PRG01310
C     WRITE(6,750)                                                          PRG01320
      DO 30 I=1,M                                                           PRG01330
      T=TIME(I)-TIME(I-1)                                                   PRG01340
      SUMC1  = SUMC1  + T*(C1F(I) + C1F(I-1))/2.                            PRG01350
      SUMC2  = SUMC2  + T*(C2F(I) +C2F(I-1))/2.                             PRG01360
      SUMC22 = SUMC22 + T*(C22F(I) +C22F(I-1))/2.                           PRG01370
      SUMC3  = SUMC3  + T*(C3F(I)+C3F(I-1))/2.                              PRG01380
      SUMC33 = SUMC33 + T*(C33F(I)+C33F(I-1))/2.                            PRG01390
      SUMC4  = SUMC4  + T*(C4F(I) +C4F(I-1))/2.                             PRG01400
      SUMC44 = SUMC44 + T*(C44F(I)+C44F(I-1))/2.                            PRG01410
      SUMC5  = SUMC5  + T*(C5F(I)+C5F(I-1))/2.                              PRG01420
C     WRITE(6,800) NSAMPL(I),SUMC1,SUMC2,SUMC22,SUMC3,SUMC33,SUMC4,         PRG01430
C    +SUMC44,SUMC5                                                          PRG01440
  30  CONTINUE                                                              PRG01450
C                                                                           PRG01460
C  EVALUATE OVERALL YIELDS AND SELECTIVITIES                                PRG01470
C                                                                           PRG01480
      TOTFD   = FMEOH*TIME(M)                                               PRG01490
C                                                                           PRG01500
C    YIELDS                                                                 PRG01510
C                                                                           PRG01520
      YC1  = SUMC1/TOTFD*100.                                               PRG01530
      YC2  = SUMC2/TOTFD*100.                                               PRG01540
      YC22 = SUMC22/TOTFD*100.                                              PRG01550
      YC3  = SUMC3/TOTFD*100.                                               PRG01560
      YC33 = SUMC33/TOTFD*100.                                              PRG01570
      YC4  = SUMC4/TOTFD*100.                                               PRG01580
      YC44 = SUMC44/TOTFD*100.                                              PRG01590
      YC5  = SUMC5/TOTFD*100.                                               PRG01600
C                                                                           PRG01610
      TOTHC = YC1+YC2+YC3+YC4+YC5+YC22+YC33+YC44                            PRG01620
C                                                                           PRG01630
C    SELECTIVITIES                                                          PRG01640
C                                                                           PRG01650
```

```
      C22S = YC22/TOTHC*100.                                            PRG01660
      C33S = YC33/TOTHC*100.                                            PRG01670
      C44S = YC44/TOTHC*100.                                            PRG01680
      C1S = YC1/TOTHC*100.                                              PRG01690
      C2S = YC2/TOTHC*100.                                              PRG01700
      C3S = YC3/TOTHC*100.                                              PRG01710
      C4S = YC4/TOTHC*100.                                              PRG01720
      C5S = YC5/TOTHC*100.                                              PRG01730
C                                                                       PRG01740
C     PRINT RESULTS                                                     PRG01750
C                                                                       PRG01760
      WRITE(6,900)                                                      PRG01770
      WRITE(6,910)YC22,C22S                                             PRG01780
      WRITE(6,920)YC33,C33S                                             PRG01790
      WRITE(6,930)YC44,C44S                                             PRG01800
      WRITE(6,940)                                                      PRG01810
      WRITE(6,950)YC1,C1S                                               PRG01820
      WRITE(6,960)YC2,C2S                                               PRG01830
      WRITE(6,970)YC3,C3S                                               PRG01840
      WRITE(6,980)YC4,C4S                                               PRG01850
      WRITE(6,990)YC5,C5S                                               PRG01860
C                                                                       PRG01870
 99   FORMAT(10X,'CATALYST       : Z7/Ba 5.2 Impregnation '             PRG01880
     +/10X,'TEMPERATURE    :',F6.1,' C'/10X,'WHSV',11X,':',F5.2,' HR'/  PRG01890
     +10X,'TOTAL RUN TIME : ',F7.2,' HR'/)                              PRG01900
 100  FORMAT(/10X,'TABLE   : GAS ANALYSIS FOR HYDROCARBONS'              PRG01910
     +//)                                                               PRG01920
 103  FORMAT(/5X,'TABLE   : GAS ANALYSIS FOR OLEFINS (INPUT DATA)'//)   PRG01930
 105  FORMAT(/5X,'TABLE   : GAS ANALYSIS FOR ALKANES (INPUT DATA)'//)   PRG01940
 110  FORMAT(5X,'SAMPLE',4X,'TIME',4X,'C2=',6X,'C3=',                   PRG01950
     +7X,'C4='/7X,'NO.',5X,'(HR)'/)                                     PRG01960
 120  FORMAT(5X,'SAMPLE',4X,'TIME',6X,'C1',7X,'C2',8X,'C3',8X,          PRG01970
     +'C4',9X,'C5'/15X,'(HR)')                                          PRG01980
 130  FORMAT(5X, I3, 6(4X,F6.2))                                        PRG01990
 135  FORMAT(9X, I3,13(4X,F6.2))                                        PRG02000
 140  FORMAT(5X,I3,7(4X,F6.2))                                          PRG02010
 150  FORMAT(10X,'AVERAGE GASRATE =',F6.2,' LIT/HR'/)                   PRG02020
 200  FORMAT(10X,F6.3)                                                  PRG02030
 300  FORMAT(5X,8(3X,F7.3))                                             PRG02040
 350  FORMAT(//5X,'FLOWRATES')                                          PRG02050
 700  FORMAT(10X,I2,8(3X,F6.2 ))                                        PRG02060
 710  FORMAT(/10X,'TABLE   : POINT YIELDS FOR HYDROCARBONS'/)           PRG02070
 715  FORMAT(//5X,'TABLE   : POINT YIELDS FOR OLEFINS'/)                PRG02080
 720  FORMAT(//5X,'TABLE   : POINT YIELDS FOR ALKANES'/)                PRG02090
 730  FORMAT(8X,'SAMPLE',4X,'TIME',6X,'C2=',5X,'C3=',5X,'C4=',5X,       PRG02100
     +'TOTAL'/10X,'NO.',4X,'(HR)'/)                                     PRG02110
 740  FORMAT(8X,'SAMPLE',3X,'TIME',6X,'C1',7X,'C2',7X,'C3',7X,          PRG02120
     +'C4',7X,'C5',5X,'TOTAL'/10X,'NO.',4X,'(HR)'/)                     PRG02130
 745  FORMAT(8X,'SAMPLE',4X,'TIME',7X,'C2=',7X,'C3=',7X,'C4=',7X,       PRG02140
     +'C1',8X,'C2',8X,'C3',8X,'C4',8X,'C5'/10X,'NO.',4X,'(HR)')        PRG02150
 747  FORMAT(8X,'SAMPLE',4X,'TIME',7X,'C2=',7X,'C3=',7X,'C4=',7X,       PRG02160
     +'C1',8X,'C2',8X,'C3',8X,'C4',8X,'C5',7X,'TOTAL',5X,'TOTAL'       PRG02170
     +/10X,'NO.',4X,'(HR)',86X,'OLEFINS',3X,'ALKANES'/)                 PRG02180
 748  FORMAT(/11X,'TIME',4X,'TOTAL',5X,'TOTAL'/                         PRG02190
     +11X,'(HR)',4X,'OLEFINS',3X,'ALKANES'/)                            PRG02200
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750   FORMAT(//5X,'AREAS'/)                                          PRG02210
800   FORMAT(5X,I2,8(2X,E10.3))                                      PRG02220
900   FORMAT(/10X,'OVERALL COMPONENT YIELDS AND SELECTIVITIES:'/      PRG02230
     +//9X,'COMPONENT',3X,'YIELD(%)',3X,'SELECTIVITY(%)'//10X,       PRG02240
     +'OLEFINS:'/)                                                   PRG02250
910   FORMAT(14X,'C2= ',2(4X,F6.3))                                  PRG02260
920   FORMAT(14X,'C3= ',2(4X,F6.3))                                  PRG02270
930   FORMAT(14X,'C4= ',2(4X,F6.3)/)                                 PRG02280
940   FORMAT(10X,'ALKANES:'/)                                        PRG02290
950   FORMAT(14X,'C1  ',2(4X,F6.3))                                  PRG02300
960   FORMAT(14X,'C2  ',2(4X,F6.3))                                  PRG02310
970   FORMAT(14X,'C3  ',2(4X,F6.3))                                  PRG02320
980   FORMAT(14X,'C4  ',2(4X,F6.3))                                  PRG02330
990   FORMAT(14X,'C5  ',2(4X,F6.3))                                  PRG02340
      END                                                            PRG02350
```